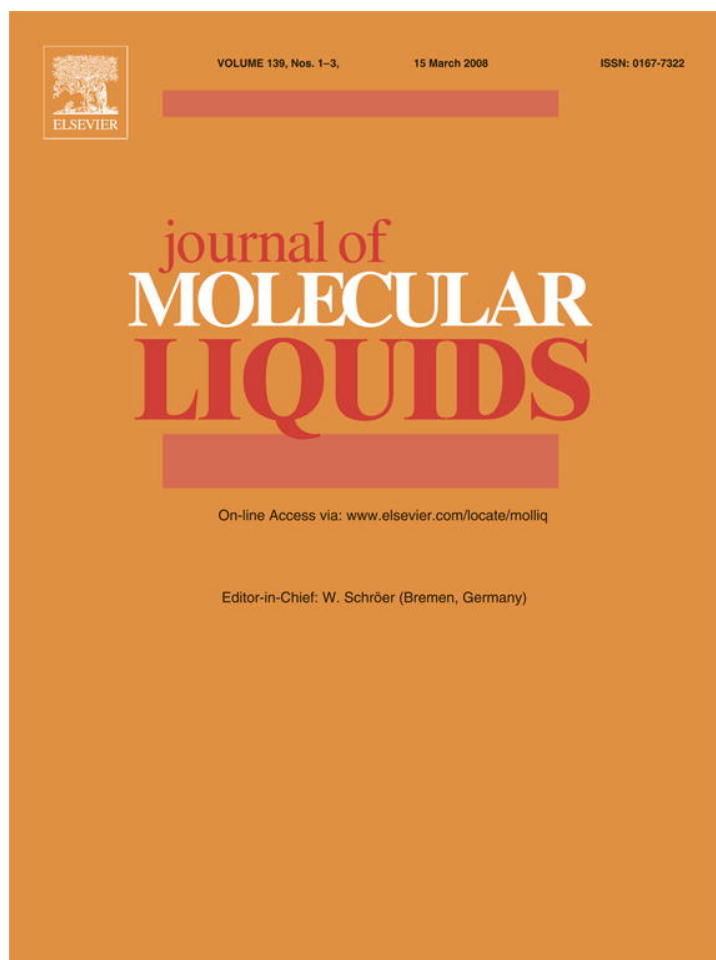


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Viscosimetric behaviour of *n*-alkanols with triethylene glycol monomethyl ether at different temperatures

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Abstract

The thermodynamic functions of activation for viscous flow have been evaluated from the dynamic viscosity values of binary mixtures considering Eyring's transition state theory. Kinematic viscosities and densities of binary mixtures containing triethylene glycol monomethyl ether+(2-propanol or 2-butanol or 2-pentanol) over the whole mole fraction range of triethylene glycol monomethyl ether, at four different temperatures and atmospheric pressure were determined. Viscosity deviations and excess Gibbs energies of activation for viscous flow were calculated. All the values of viscosity deviations are negative, at all temperatures. The molar enthalpy of activation for viscous flow and molar entropy of activation for viscous flow functions were obtained. These functions with concentration of the triethylene glycol monomethyl ether show a minimum. These mixtures show a similar behaviour to that of the hydrocarbon–alkanol mixtures. The Grunberg–Nissan and Katti–Chaudrhi parameters were calculated and viscosity data were analyzed on the basis of their treatment.

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1. Introduction

The system of derivatives of ethylene glycol polyether+ other self-associated component has been a research subject to analyse thermodynamic properties and to understand the interaction between components with self-association and the possibility of cross-association [1,2]. The triethylene glycol monomethyl ether is a self-associated component because it has in its chemical structure not only the possibility of association with different oxygen atoms of the polyether acting as proton acceptor but also interactions between their OH terminal group and oxygen ether atoms. The triethylene glycol monomethyl ether is a physical solvent which has a strong affinity for CO₂ [3] and can be used for the removal of acid gases from mixtures of gases [4].

This paper is part of the systematic study on the thermodynamic and transport properties of binary mixtures of 1-alkanol and 2-alkanol with polyether [5–7]. We report about the

viscosities and densities of binary solutions of triethylene glycol monomethyl ether in 2-propanol, 2-butanol and 2-pentanol at four different temperatures, between 288.15 K and 318.15 K, over the entire mole fraction range of triethylene glycol monomethyl ether at atmospheric pressure.

The average molar Gibbs energy of activation for viscous flow is calculated using the rate process Eyring theory. On the other hand, values of the molar enthalpy and molar entropy of activation for viscous flow functions are reported in this paper. The properties of viscous flow are used to discuss qualitatively the nature of interactions that occur when ether is mixed with 2-alkanols of different chain lengths.

2. Experimental section

2.1. Materials

2-propanol (2-PR) and 2-butanol (2-BU), Merck, and 2-pentanol (2-PE), Fluka pro-analysis, were carefully dried with molecular sieves and used without later purification. Triethylene

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Table 1

Comparison of experimental data of density (ρ), and viscosity (η) with literature data for pure components at 298.15 K

Components	ρ (g cm ⁻³)		η (mPa s)	
	Experimental	Literature	Experimental	Literature
2-Propanol	0.7809	0.78126 ^a 0.7809 ^b	2.089	2.0436 ^a 2.045 ^b
2-Butanol	0.8023	0.80241 ^a 0.80240 ^c	3.150	2.998 ^a
2-Pentanol	0.8047	0.8054 ^a 0.80501 ^c	3.381	3.510 ^{d, a} 3.273 ^c
TRIEGMME	1.0414	1.04524 ^f 1.04304 ^g 1.0430 ^h	6.318	6.253 ^f 6.240 ^g 6.586 ^h

^a Ref. [8].

^b Ref. [10].

^c Ref. [11].

^d Extrapolated.

^e Ref. [12].

^f Ref. [13] >97% pure.

^g Ref. [14] >97% pure.

^h Ref [15] >97% pure.

glycol monomethyl ether (TRIEGMME), 95%, Aldrich, with 2% of impurities of each of the corresponding ether of diethylene glycol and with ~ 2% of the ones that correspond to tetraethylene glycol according to Aldrich Chemical Co., was used without later purification and was also kept over molecular sieves. Their physical properties were checked with the literature data and their values are presented in Table 1 [8,10–15].

A graph to compare the viscosity values obtained at four temperatures with TRIEGMME, 95%, Aldrich, and the viscosity values of reference [14] obtained with a TRIEGMME, product, >97%, Fluka, between 25 and 70 °C, was included in Fig. 1. The coincidence of values in the temperature zone between 25 and 50 °C could be explained by a compensation effect of impurities. It was found out that the dynamic viscosity of polyether of ethylene glycol increases with the CH₂CH₂O group number

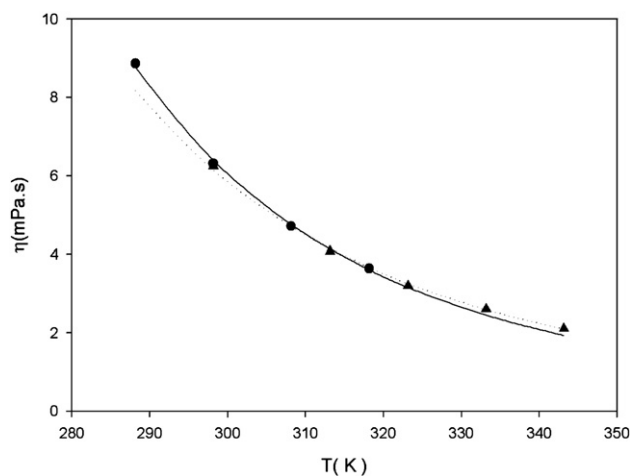


Fig. 1. Comparison of experimental dynamic viscosity data at different temperatures with dynamic viscosity data of reference [14]. (●) this work. (▲) reference [14]. Curve (--- this work; ——— reference [14]) were drawn using $\eta = \exp(a + b/T)$ equation.

Table 2

Values of parameters in Eq. (2) and their standard deviations for dynamic viscosity (mPa s) at different temperatures

TRIEGMME+2-PR				
Parameter	288.15 K	298.15 K	308.15 K	318.15 K
b0	2.80±0.03	2.09±0.02	1.55±0.01	1.19±0.01
b1	0.84±0.30	1.26±0.20	1.34±0.10	1.35±0.06
b2	8.64±0.74	5.06±0.50	3.18±0.25	2.01±0.14
b3	-3.40±0.48	-2.05±0.33	-1.34±0.17	-0.90±0.09
σ	0.05	0.04	0.04	0.01

TRIEGMME+2-BU

Parameter	288.15 K	298.15 K	308.15 K	318.15 K
b0	4.50±0.08	3.08±0.03	2.16±0.01	1.57±0.01
b1	-5.47±0.85	-2.29±0.33	-0.52±0.11	0.37±0.04
b2	17.3±2.1	9.70±0.80	5.31±0.26	2.82±0.11
b3	-7.55±1.37	-4.18±0.52	-2.24±0.17	-1.12±0.07
σ	0.06	0.05	0.02	0.01

TRIEGMME+2-PE

Parameter	288.15 K	298.15 K	308.15 K	318.15 K
b0	4.94±0.07	3.33±0.03	2.32±0.01	1.67±0.01
b1	-5.60±0.74	-2.39±0.28	-0.61±0.09	0.28±0.06
b2	15.7±1.8	8.91±0.68	4.79±0.21	2.51±0.14
b3	-6.20±1.20	-3.54±0.45	-1.78±0.14	-0.82±0.09
σ	0.06	0.03	0.01	0.01

according to Comuñas et al. [16], in a study related to pressure and temperature effect over polyethers of ethylene glycol viscosity. Thus we could think that the content of ethers of diethylene glycol reduces the viscosity values and the tetraethylene glycol impurities act in the apposite sense. Differences among values are greater at higher or lower temperatures than the zone shown.

2.2. Equipment

Kinematic viscosity measurement of pure liquids and their mixtures were made with an automatic Schott Gerate AVS 400 viscosity-measuring system equipped with a series of Ubbelohde viscosimeters, the range of the flow times was 200–800 s. In all the cases the experiments were generally performed at least with five replicates for each composition and at each temperature and the results were averaged. A thermostated bath constant to ± 0.02 K was used and the temperatures were read from calibrated thermometers. The overall experimental error in kinematic viscosity was approximately ± 0.003 cSt.

Dynamic viscosity, η , was calculated with the following equation:

$$\eta = k(t_m - f)\rho \quad (1)$$

where t_m is time, k is the viscosimeter constant, f is the Hagenbach correction factor, and ρ the density.

Densities were determined with an Anton Paar digital densimeter, model DMA 45. Calibration was carried out with air and doubly distilled water. The estimated error in the density measurement was approximately $\pm 2 \cdot 10^{-4}$ g cm⁻³.

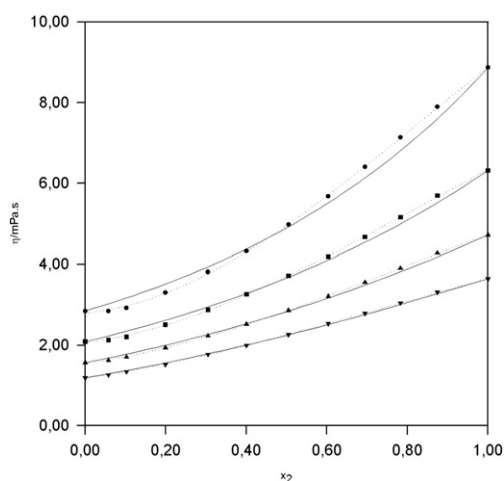


Fig. 2. The experimental viscosity η against x_2 at different temperatures: (●) 288.15 K, (■) 298.15 K, (▲) 308.15 K, (▼) 318.15 K. The prediction viscosity for Grunberg–Nissan equation solid line —, the calculated viscosity values of polynomial equation: — line. TRIEGMME+2-PR system.

All weightings were made on a Mettler H20T balance and the estimated error in mole fraction was $\pm 1.4 \cdot 10^{-4}$.

3. Results and discussion

The dynamic viscosity (η) and the density (ρ) values of solutions of TRIEGMME in 2-PE, 2-BU, or 2-PE are included in Electronic Supplement (E.S.) (Tables 1, 2, and 3).

The dependence of dynamic viscosity on mole fraction of polyether was studied with a polynomial equation:

$$\eta = \sum_{i=0}^n b_i x_2^i \quad (2)$$

Table 2 presents the parameters of Eq. (2).

Figs. 2, 3 and 4 show experimental dynamic viscosities against mole fraction for the TRIEGMME+2-PR, TRIEGMME+2-BU,

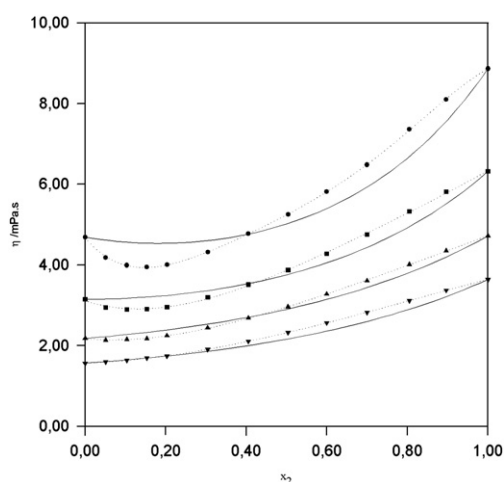


Fig. 3. The experimental viscosity η against x_2 at different temperatures: (●) 288.15 K, (■) 298.15 K, (▲) 308.15 K, (▼) 318.15 K. The prediction viscosity for Grunberg–Nissan equation solid line —, the calculated viscosity values of polynomial equation: — line. TRIEGMME+2-BU system.

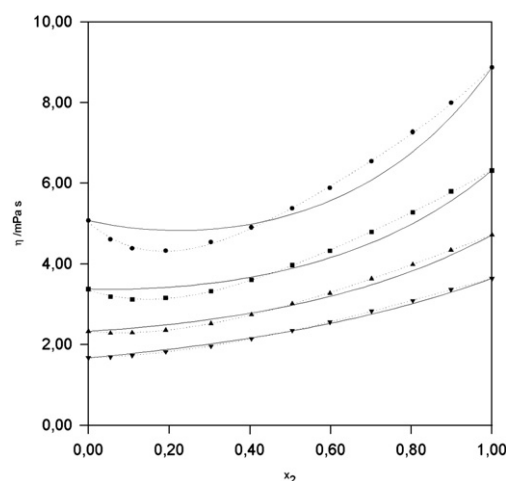


Fig. 4. The experimental viscosity η against x_2 at different temperatures: (●) 288.15 K, (■) 298.15 K, (▲) 308.15 K, (▼) 318.15 K. The prediction viscosity for Grunberg–Nissan equation solid line —, the calculated viscosity values of polynomial equation: — line. TRIEGMME+2-PE system.

TRIEGMME+2-PE systems and the fitted values for polynomial equation also show predicted values by Grunberg–Nissan relation [17].

Dynamic viscosity values for TRIEGMME+2-PR mixtures increase with an increasing concentration of triethylene glycol monomethyl ether at all temperatures. The values of viscosities for TRIEGMME+2-BU and TRIEGMME+2-PE systems (at 288.15 K, 298.15 K and 308.15 K) slightly decrease in relation to the viscosity of pure alcohol with the increase of concentration of triethylene glycol monomethyl ether. The decrease just mentioned presents a minimum that is a function of the temperature, and after this minimum it increases. The dynamic viscosity minimum disappears at higher temperature for TRIEGMME+2-BU and TRIEGMME+2-PE systems.

Viscosimetric behaviours similar to TRIEGMME+2-BU and TRIEGMME+2-PE systems, with a minimum of viscosity, are characteristic of systems in which complexes are not formed and one component is associated in a pure state [18]. Those behaviours were also observed in binary systems containing tetraethylene glycol dimethyl ethers+1-alkanol [3].

The experimental density values are fitted by a polynomial equation:

$$\rho = \sum_{i=0}^n c_i x_2^i \quad (3)$$

Table 3 presents the parameters of Eq. (3). Density values for all binary mixtures increase with increases of TRIEGMME concentration.

From Eyring's theory, the average molar Gibbs energy of activation for viscous flow of solution, ΔG^* (J mol^{-1}), is given [19] by:

$$\Delta G^* = RT \ln \left(\frac{V_{1,2}\eta}{h N} \right) \quad (4)$$

Table 3
Values of parameters in Eq. (3) and their standard deviations for density (g cm^{-3}) at different temperatures

TRIEGMME+2-PR				
Parameter	288.15 K	298.15 K	308.15 K	318.15 K
c0	0.7899 ± 5.10^{-4}	0.7807 ± 5.10^{-4}	0.7723 ± 5.10^{-4}	0.7633 ± 5.10^{-4}
c1	0.515 ± 7.10^{-3}	0.513 ± 5.10^{-3}	0.513 ± 5.10^{-3}	0.512 ± 5.10^{-3}
c2	-0.390 ± 1.10^{-3}	-0.390 ± 1.10^{-3}	-0.390 ± 1.10^{-3}	-0.390 ± 1.10^{-3}
c3	0.137 ± 9.10^{-3}	0.136 ± 9.10^{-3}	0.136 ± 9.10^{-3}	0.135 ± 9.10^{-3}
σ	0.0002	0.0003	0.0003	0.0003
TRIEGMME+2-BU				
Parameter	288.15 K	298.15 K	308.15 K	318.15 K
c0	0.8103 ± 2.10^{-4}	0.8023 ± 2.10^{-4}	0.7942 ± 2.10^{-4}	0.7851 ± 2.10^{-4}
c1	0.389 ± 2.10^{-3}	0.387 ± 2.10^{-3}	0.387 ± 2.10^{-3}	0.388 ± 2.10^{-3}
c2	-0.206 ± 5.10^{-3}	-0.203 ± 5.10^{-3}	-0.204 ± 5.10^{-3}	-0.205 ± 5.10^{-3}
c3	0.057 ± 3.10^{-3}	0.055 ± 3.10^{-3}	0.056 ± 3.10^{-3}	0.057 ± 3.10^{-3}
σ	0.0003	0.0004	0.0004	0.0005
TRIEGMME+2-PE				
Parameter	288.15 K	298.15 K	308.15 K	318.15 K
c0	0.8128 ± 9.10^{-5}	0.8050 ± 1.10^{-4}	0.7966 ± 1.10^{-4}	0.7881 ± 1.10^{-4}
c1	0.3248 ± 9.10^{-4}	0.325 ± 1.10^{-3}	0.325 ± 1.10^{-3}	0.325 ± 1.10^{-3}
c2	-0.107 ± 2.10^{-3}	-0.108 ± 3.10^{-3}	-0.109 ± 3.10^{-3}	-0.110 ± 3.10^{-3}
c3	0.019 ± 2.10^{-3}	0.020 ± 2.10^{-3}	0.027 ± 2.10^{-3}	0.021 ± 2.10^{-3}
σ	0.0001	0.0001	0.0001	0.0001

where R is the gas constant, T is the absolute temperature, $V_{1,2}$ is the mean molar volume of the solution, h is the Planck's constant and N is the Avogadro's constant.

The molar Gibbs energy of activation for viscous flow values of solutions of TRIEGMME in 2-propanol, 2-butanol and 2-pentanol are included in Electronic Supplement (Table 4). The molar Gibbs energy of activation for viscous flow values for TRIEGMME+2-PR system increases when concentration of TRIEGMME increases at all temperatures. For TRIEGMME+2-BU and TRIEGMME+2-PE systems there is only an increase at 308.15 K and 318.15 K. The molar Gibbs function of activation for viscous flow of the later systems at 288.15 K and 298.15 K presents a minimum in the zone rich in alkanol and then molar Gibbs energy of activation for viscous flow values increases.

The molar enthalpy and entropy of activation for viscous flow values, obtained using Eyring equation and Gibbs–Helmholtz relation, are positive. Fig. 5 presents a plot of the molar Gibbs energy of activation for viscous flow and the molar enthalpy and entropic contribution of activation for viscous

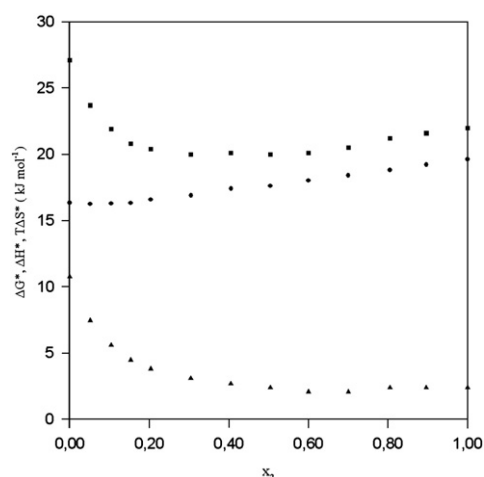


Fig. 5. The molar Gibbs energy of activation for viscous flow, the enthalpic, and entropic of activation for viscous flow contributions against x_2 of TRIEGMME+2-BU system. (●) ΔG^* , (■) ΔH^* , and (▲) $T\Delta S^*$.

flow against triethylene glycol monomethyl ether mole fraction of TRIEGMME+2-BU system. The molar enthalpy and entropy of activation for viscous flow values versus concentration of triethylene glycol monomethyl ether show a minimum for the three systems. All the systems studied present similar plots.

The decrease of the molar enthalpy of activation for viscous flow in the zone of high concentration of alkanol should be noted and understood as that energy of activation for viscous flow related to the work required to form a hole in the liquid for it to flow [19]. This work in the mixture is smaller than the one required in the pure alkanol. The molar enthalpy magnitude of activation for viscous flow is higher than $T\Delta S^*$ values. It may be concluded that the energetic contribution corresponding to the molar enthalpy of activation for viscous flow is more important than the entropic contribution terms to the molar Gibbs energy of activation for viscous flow values.

The dynamic viscosity deviation ($\Delta\eta$) is calculated by equation

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (5)$$

where $\Delta\eta$, η , η_1 and η_2 are the viscosity deviation, mixture viscosity and pure component viscosity, respectively.

On the basis of the theory of absolute reaction rates, the excess Gibbs energies of activation for viscous flow, ΔG^{*E} , were calculated as follows:

$$\Delta G^{*E} = RT \left[\ln \left(\frac{V_{1,2}\eta}{V_2\eta_2} \right) - x_1 \ln \left[\frac{V_1\eta_1}{V_2\eta_2} \right] \right] \quad (6)$$

where $V_{1,2}$ is the mean molar volume and V_1 , V_2 , η_1 and η_2 are the molar volume and viscosity of pure components, respectively.

The values of the dynamic viscosity deviations for TRIEGMME+2-PR, TRIEGMME+2-BU and TRIEGMME+2-PE systems are included in Electronic Supplement (Table 5). The dynamic viscosity deviation and the excess Gibbs energies

Table 4

Values of parameters and standard deviations in Redlich–Kister equation for dynamic viscosity deviations ($\Delta\eta/\text{mPa s}$) and standard deviations of deviation in viscosity $\sigma(\Delta\eta)$ at different temperatures

TRIEGMME+2-PR				
Parameters	288.15 K	298.15 K	308.15 K	318.15 K
A0	-3.68 ± 0.01	-2.02 ± 0.01	-1.17 ± 0.01	-0.65 ± 0.01
A1	-1.16 ± 0.05	-0.58 ± 0.06	-0.45 ± 0.03	-0.33 ± 0.03
A2	1.34 ± 0.15			
A3	-2.07 ± 0.12	-1.73 ± 0.16	-0.87 ± 0.07	-0.45 ± 0.07
A4	-2.51 ± 0.27			
σ	0.004	0.006	0.002	0.002

TRIEGMME+2-BU				
Parameters	288.15 K	298.15 K	308.15 K	318.15 K
A0	-6.14 ± 0.04	-3.48 ± 0.02	-1.98 ± 0.01	-1.14 ± 0.01
A1	-2.22 ± 0.16	-1.46 ± 0.08	-0.92 ± 0.05	-0.57 ± 0.02
A2	-2.66 ± 0.17	-0.92 ± 0.08	-0.28 ± 0.06	0.09 ± 0.04
A3	-5.39 ± 0.39	-2.21 ± 0.19	-0.67 ± 0.13	
σ	0.01	0.007	0.005	0.004

TRIEGMME+2-PE				
Parameters	288.15 K	298.15 K	308.15 K	318.15 K
A0	-6.52 ± 0.01	-3.63 ± 0.02	-2.13 ± 0.02	-1.28 ± 0.01
A1	-2.51 ± 0.05	-1.49 ± 0.10	-0.80 ± 0.07	-0.42 ± 0.03
A2	-1.76 ± 0.15	-1.00 ± 0.11	-0.20 ± 0.08	0.07 ± 0.06
A3	-2.26 ± 0.12	-1.13 ± 0.24	-0.37 ± 0.17	
A4	-2.10 ± 0.26			
σ	0.004	0.009	0.007	0.006

Table 5

Values of parameters and standard deviations in Redlich–Kister equation for excess Gibbs energies of activation for viscous flow ($\Delta G^{*E}/\text{kJ mol}^{-1}$) and standard deviations of deviation in excess Gibbs energies of activation for viscous flow $\sigma(\Delta G^{*E})$ at different temperatures

TRIEGMME+2-PR				
Parameters	288.15 K	298.15 K	308.15 K	318.15 K
A0	0.48 ± 0.04	0.80 ± 0.04	1.11 ± 0.02	1.45 ± 0.02
A1	-0.71 ± 0.17	-0.46 ± 0.14	-0.30 ± 0.08	-0.11 ± 0.09
A2	-0.97 ± 0.20	-0.69 ± 0.17	0.45 ± 0.09	-0.26 ± 0.11
A3	-1.59 ± 0.43	-1.38 ± 0.37	-0.96 ± 0.20	-0.67 ± 0.24
σ	0.003	0.004	0.002	0.003

TRIEGMME+2-BU				
Parameters	288.15 K	298.15 K	308.15 K	318.15 K
A0	-1.62 ± 0.02	-1.05 ± 0.02	-0.47 ± 0.01	0.06 ± 0.01
A1	-1.76 ± 0.07	-1.49 ± 0.06	-1.18 ± 0.05	-0.84 ± 0.03
A2	-1.94 ± 0.08	-1.25 ± 0.07	-0.77 ± 0.05	-0.25 ± 0.06
A3	-2.47 ± 0.17	-1.49 ± 0.15	-0.67 ± 0.12	
σ	0.005	0.005	0.005	0.005

TRIEGMME+2-PE				
Parameters	288.15 K	298.15 K	308.15 K	318.15 K
A0	-1.98 ± 0.01	-1.39 ± 0.01	-0.87 ± 0.01	-0.39 ± 0.02
A1	-1.82 ± 0.05	-1.52 ± 0.06	-1.13 ± 0.06	-0.77 ± 0.03
A2	-1.59 ± 0.05	-1.02 ± 0.07	-0.52 ± 0.07	-0.18 ± 0.07
A3	-1.05 ± 0.11	-0.68 ± 0.15	-0.32 ± 0.14	
σ	0.002	0.006	0.006	0.007

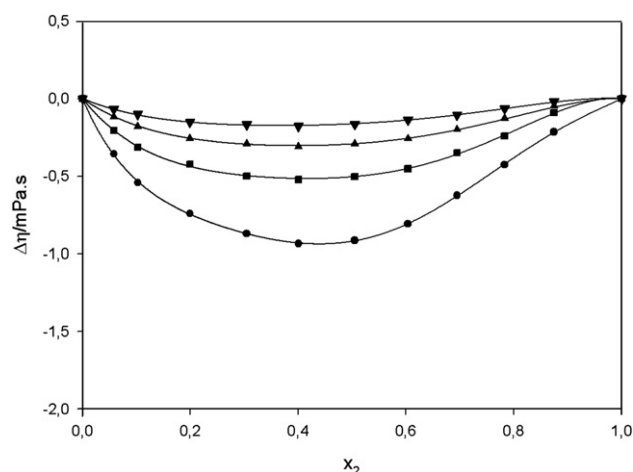


Fig. 6. The viscosity deviation against x_2 at different temperatures: (●) 288.15 K, (■) 298.15 K, (▲) 308.15 K, (▼) 318.15 K. Solid line — calculated viscosity deviation with Redlich–Kister equation: TRIEGMME+2-PR system.

of activation for viscous flow are correlated by Redlich–Kister equation [20].

$$\Delta F = x_1 x_2 \sum_{i=0}^{i=k} A_i (x_1 - x_2)^i \quad (7)$$

where ΔF is $\Delta\eta$ in mPa s or ΔG^{*E} in kJ mol^{-1} .

Tables 4 and 5 present fitted parameter values for the dynamic viscosity deviation and the excess Gibbs energies of activation for viscous flow functions, respectively.

Figs. 6, 7 and 8 show the dynamic viscosity deviations versus mole fractions of solutions of triethylene glycol monomethyl ether in 2-propanol, 2-butanol, or 2-pentanol at different temperatures. In all cases, the values of dynamic viscosity deviations are negative. In the curve minimum of the dynamic viscosity deviations versus mole fractions, dynamic viscosity deviations values are near -1.0 mPa s in the case of TRIEGMME+2-PR system. For the TRIEGMME+2-BU and

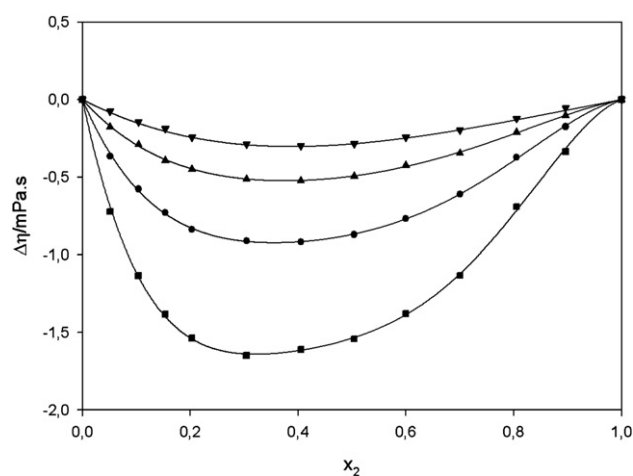


Fig. 7. The viscosity deviation against x_2 at different temperatures: (●) 288.15 K, (■) 298.15 K, (▲) 308.15 K, (▼) 318.15 K. Solid line — calculated viscosity deviation with Redlich–Kister equation for TRIEGMME+2-BU system.

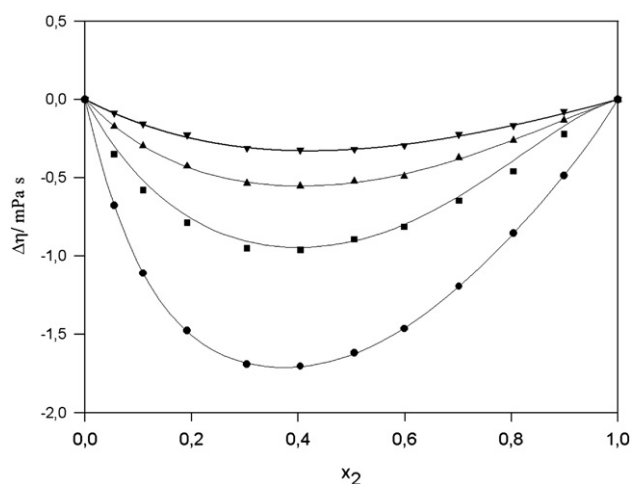


Fig. 8. The viscosity deviation against x_2 at different temperatures: (●) 288.15 K, (■) 298.15 K, (▲) 308.15 K, (▼) 318.15 K. Solid line — calculated viscosity deviation with Redlich–Kister equation for TRIEGMME+2-PE system.

TRIEGMME+2-PE systems values are near -2.0 mPa s. In these systems the curve minimum at mole fraction values is smaller than 0.4 as opposed to what happens in the TRIEGMME+2-PR system where the curve minimum is between 0.4 and 0.5 mole fraction values.

Plots of this type were observed in systems in which one component (1-alkanol, 2-alkanol) is associated [5,12,21]. Negative viscosity deviations occur where dispersion forces are primarily responsible for interaction. These mixtures show a similar behaviour to that of the hydrocarbon–alkanol mixtures, and the hydrogen bond rupture is produced; then the viscosities of the liquid mixtures have a minimum [9,10,22]. The hydrogen bond breaking was observed in other systems containing glycol derivative+1-alkanol where the excess molar enthalpies of the systems mentioned are positive [6].

Reddy et al. [23] have determined excess enthalpies of mixtures of 2-methoxyethanol with alcohols at 25 °C in which they show that the predominant effect is the breaking of the hydrogen bond among like molecules in the alcohols studied except methanol where formation of hydrogen bond are shown to be prevailing. On the other hand, they found that lower alcohols interact more strongly than higher alcohols in the mixtures. This effect could be due to steric hindrance of the methyl group in higher alcohols. In TRIEGMME+2-BU and TRIEGMME+2-PE diluted mixtures, the increment of the steric hindrance could explain the presence of a minimum in the graphs of the dynamic viscosity with the mole fraction.

The values of the excess Gibbs energies of activation for viscous flow are negative for TRIEGMME+2-BU and TRIEGMME+2-PE systems and sigmoid for TRIEGMME+2-PR mixtures.

Fig. 9 shows the dynamic viscosity deviations, at 298.15 K and $x_2 = 0.5$ versus carbon atom number of solutions of triethylene glycol monomethyl ether in 2-PR, 2-BU, or 2-PE. The negative magnitude of deviations increases with the increase of the chain length from three to four atoms of carbon in the 2-alcohols. But TRIEGMME+2-BU and TRIEGMME+2-PE systems have proximate values of viscosity deviations and a higher negative magnitude than TRIEGMME+2-PR mixture.

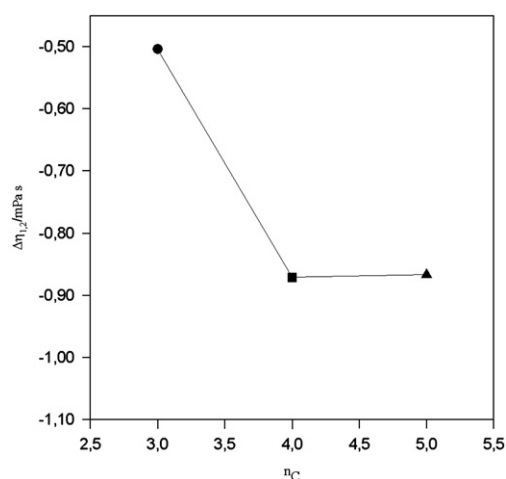


Fig. 9. The viscosity deviation at 298.15 K and $x_2=0.5$ against carbon atom number, for: (●) TRIEGMME+2-PR system, (■) TRIEGMME+2-BU system, (▲) TRIEGMME+2-PE system.

Viscosity–mole fraction data pairs of the mixtures were used to test the empirical one-parameter relation proposed by Grunberg and Nissan [17] and to test also the relation of Katti–Chaudrhi [24].

The Grunberg–Nissan equation is based on the Arrhenius equation for the dynamic viscosity of a mixture:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d \quad (8)$$

where the parameter “d”, which is independent of the mixture composition and the characteristics of each system, can be either positive or negative and represents a measure of the

Table 6
Values of parameters and standard deviations of Grunberg–Nissan and Katti–Chaudrhi equations

TRIEGMME+2-PR				
T/K	288.15 K	298.15 K	308.15 K	318.15 K
d (G–N)	-0.104 ± 0.076	0.036 ± 0.056	0.164 ± 0.038	0.297 ± 0.024
σ	0.04	0.03	0.02	0.03
W_{vis} (K–C)	350 ± 167	701 ± 124	1049 ± 83	1422 ± 48
σ	0.04	0.03	0.02	0.01
TRIEGMME+2-BU				
T/K	288.15 K	298.15 K	308.15 K	318.15 K
d (G–N)	-1.005 ± 0.150	-0.689 ± 0.109	-0.399 ± 0.074	-0.149 ± 0.042
σ	0.09	0.06	0.04	0.03
W_{vis} (K–C)	-2050 ± 352	-1340 ± 261	-649 ± 179	-14 ± 101
σ	0.09	0.06	0.06	0.02
TRIEGMME+2-PE				
T/K	288.15 K	298.15 K	308.15 K	318.15 K
d (G–N)	-1.008 ± 0.118	-0.702 ± 0.089	-0.445 ± 0.060	-0.231 ± 0.036
σ	0.07	0.05	0.03	0.02
W_{vis} (K–C)	-2211 ± 284	-1560 ± 217	-956 ± 150	-424 ± 92
σ	0.07	0.05	0.03	0.02

intermolecular interactions among unlike molecules. Table 6 presents “d” parameter values and the standard deviation values calculated for the three systems studied.

Nigam et al. [25] have suggested that different “d” values of Grunberg–Nissan equation may be taken as indicative of specific interactions; large positive “d” values indicate strong specific interactions, small positive “d” values indicate weak specific interactions whereas large negative “d” values indicate no specific interaction between molecules.

Table 6 shows the parameter “d” values at different temperature for the three study systems. The “d” values for the TRIEGMME+2-PR go from the negative value at 288.15 K to positive values at 298.15 K, 308.15 K, and 318.15 K. The same upward trend with the temperature can be observed with “d” negative values for the TRIEGMME+2-BU and TRIEGMME+2-PE systems. Following Nigam et al. [25] we could find the presence of weak specific interactions. Considering “d” parameter as a measure of resulting interactions, the breaking of hydrogen bonds could be the specific interaction taken into account.

Figs. 2, 3, and 4 show the predicted viscosity values by the Grunberg–Nissan equation. For the TRIEGMME+2-PR systems the Grunberg–Nissan relation predicts correct viscosity values, but for TRIEGMME+2-BU, TRIEGMME+2-PE systems the predicted values are correct only at greater temperatures. The relation seems adequate for systems where the dynamic viscosity values of the mixtures do not have a minimum.

Katti and Chaudrhi derived the following equation:

$$\ln \eta V = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + x_1 x_2 W_{\text{vis}} / (RT) \quad (9)$$

where W_{vis} is an interaction parameter and V , V_1 and V_2 are molar volume of mixture and molar volume of pure component 1 and 2. Table 6 presents the parameter W_{vis} values and the standard deviation values calculated for the systems studied. The model seems adequate for systems at higher temperature. W_{vis} values found in these systems are of different signs but coherent with the ones obtained using Grunberg–Nissan relation. Thus, positive W_{vis} is found in the TRIEGMME+2-PR system and negative W_{vis} in the other two systems.

4. Conclusions

The dynamic viscosity values of the studied mixtures show different behaviour in function of the increase of concentration of polyether. The dynamic viscosity deviation values are negative in all solutions of triethylene glycol monomethyl ether in 2-alkanol at different temperatures. These mixtures show a similar behaviour to that of the hydrocarbon–alkanol mixtures.

The dynamic viscosity deviation and the thermodynamic functions for viscous flow obtained from dynamic viscosity data show that the dispersive interactions are the main forces involved in the mixture process and also the breaking of

hydrogen bonds. The addition of polyether molecules increases the alkanol dissociation.

The Grunberg–Nissan and Katti–Chaudrhi relation seems adequate for systems where the dynamic viscosity values of the mixtures do not have a minimum. The Grunberg–Nissan and Katti–Chaudrhi equations predict similar values of viscosity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molliq.2007.12.001.

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