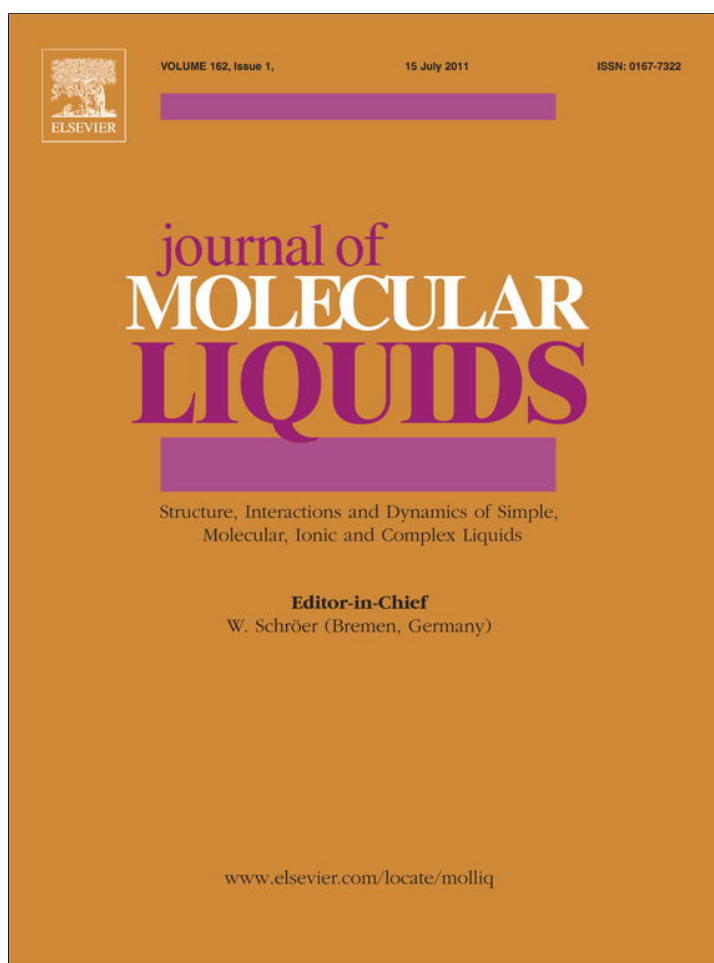


Provided for non-commercial research and education use.  
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



## Parameters of viscous flow in dilute solutions of polyalkyl glycol ethers in secondary alcohols

Silvia Aznarez<sup>b</sup>, Mercedes M.E.F. de Ruiz Holgado<sup>a</sup>, E.L. Arancibia<sup>a,\*</sup>

<sup>a</sup> INQUINOA-CONICET, Facultad de Ciencias Exactas y Tecnología, Departamento de Ingeniería de Procesos y Gestión Industrial, Laboratorio de Fisicoquímica, Av. Independencia 1800, S. M. de Tucumán, Tucumán, C. P. 4000, Argentina

<sup>b</sup> Departamento de Química, Facultad de Ingeniería, Universidad Nacional del Comahue, Buenos Aires 1400, CP 8300, Neuquén, Argentina

### ARTICLE INFO

#### Article history:

Received 30 November 2010

Received in revised form 3 February 2011

Accepted 7 February 2011

Available online 18 February 2011

#### Keywords:

Aliphatic 2-alcohol

Triethylene glycol monomethyl ether

Tetraethylene glycol dimethyl ether

Jones–Dole coefficient

Activation parameters for viscous flow

### ABSTRACT

Densities and viscosities were measured for the binary dilute mixtures of triethylene glycol monomethyl ether (TRIEGMME) in 2-alcohols (2-propanol (2-PR), 2-butanol (2-BU), and 2-pentanol (2-PE)) and tetraethylene glycol dimethyl ether (TEGDME) in 2-pentanol, at temperatures from 288.15 K to 318.15 K and in  $0 \leq x_2 \leq 0.10$  mol fraction range of the polyalkyl glycol ethers. The values of the dynamic viscosity in the TRIEGMME + 2-PR systems are more viscous than pure solvent at the work temperatures. The Jones–Dole B coefficients and  $\beta_G$  interaction parameters for viscous flow values were calculated and explain the behavior observed. The partial molar volumes at infinite dilution of solute in 2-alkanols were calculated by the parameters of viscous flow obtained in dilute solutions polyalkyl glycol ethers in 2-alkanols. The values have been compared with the values of partial molar volume at infinite dilution obtained by density measurement for both solutes in the 2-propanol, 2-butanol, and 2-pentanol.

© 2011 Elsevier B.V. All rights reserved.

### 1. Introduction

This paper is part of our systematic experimental study of thermodynamic and transport properties of mixtures polyalkyl glycol ethers with alcohols. These mixtures are complex and allow self association via inter- and intramolecular hydrogen bonds owing to the presence of –O– and –OH groups [1,2].

The interest in determination the viscosimetric properties of the dimethyl ether and the monomethyl ether of polyalkyl glycol ethers of the type  $\text{CH}_3\text{-O-}((\text{CH}_2)_2\text{-O})_n\text{-X}$  with ( $X = \text{H}$  or  $\text{CH}_3$ ) is due to the fact that these fluids can be used as absorbers in refrigeration systems and as lubricant in compressors [3]. Besides, they could also be used for the deep cleaning of air currents or gases in industrial plants [4].

The present paper reports the experimental densities and viscosity for dilute binary mixtures of triethylene glycol monomethyl ether (TRIEGMME) in 2-propanol (2-PR), 2-butanol (2-BU) and 2-pentanol (2-PE) and tetraethylene glycol dimethyl ether (TEGDME) in 2-pentanol (2-PE) at four different temperatures.

The aim of this work is to obtain information about the influence of size and shape of polyalkyl glycol ethers in the viscosimetric properties of mixtures when we go from 2-propanol, 2-butanol, and 2-pentanol. The parameter values of the interaction solute–solvent at infinite dilution of Jones–Dole coefficient (B) and the activation energetic parameters of viscous flow ( $\beta_G$ ) can be used to obtain the

molar partial volumes at infinite dilution of polyalkyl glycol ethers in alcohols. The same property was obtained by apparent molar volume of the polyalkyl glycol ethers and was compared with the obtained values of the viscosimetric properties.

Although molecular size and shape are the prominent factors of volumetric properties, they also allow getting information about the interaction in solutions and the organization of solvent molecules around solute molecules. In order to reach this aim we have used an approximation [5] that divides the partial molar volume at infinite dilution between a reference volume which is impenetrable to the solvent molecules and a term that is determined by the interaction between the solute surface and the solvent molecules around it. The nature of the interactions will be determined by the polar or non-polar character of the solute surface. The difference between the partial molar volume at infinite dilution and the reference volume allows the interpretation of the solute–solvent interactions and the organization of the solvent molecules. Several procedures have been used to obtain the intrinsic or reference volumes [6,7].

### 2. Material and methods

2-propanol (2-PR), 2-butanol (2-BU), Merck and 2-pentanol (2-PE), pro-analysis Fluka, triethylene glycol monomethyl ether (TRIEGMME), Aldrich >95%, with 2% of impurities of diethylene glycol and with approximately 2% of the ethers corresponding to tetraethylene glycol, according to Aldrich Chemical Co.. Their physical properties were checked and compared with the literature data [2]. The TEGDME (Sigma >99%) was used without later purification.

\* Corresponding author. Tel.: +54 3814364093; fax: +54 381 4363004.

E-mail address: [earancibia@herrera.unt.edu.ar](mailto:earancibia@herrera.unt.edu.ar) (E.L. Arancibia).

Tetraethylene glycol dimethyl ether (TEGDME), Sigma ≥ 99%, was used too without subsequent purifications [8]. All the reactive have been maintained over molecular sieves (4 Å).

### 3. Experimental

The measurement of kinematic viscosities was carried out with Schott-Gerate automatic equipment, AVS 400 model. The error in the measurements was 0.003 cSt. Dynamic viscosity was calculated with the equation  $\eta = k(t_m - f)\rho$ , where  $t_m$  is time,  $k$  is the viscosimeter constant,  $f$  is the Hagenbach correction factor, and  $\rho$  is the density. The densities were measured with an AP densimeter, DMA45 model, calibrated with bidistilled water and air. The error estimated in the measurements was  $\pm 0.2 \text{ kg}\cdot\text{m}^{-3}$ . A Mettler balance, HT20 model, has been used and the estimated error in mole fraction was  $1.4 \cdot 10^{-4}$ . The temperature was kept at  $\pm 0.02 \text{ K}$  with a thermostatic bath.

The dynamic viscosities ( $\eta_{1,2}$ ) and densities ( $\rho$ ) of the mixtures diluted for the systems TRIEGMME + 2-PR, TRIEGMME + 2-BU, TRIEGMME + 2-PE and DMETEG + 2-PE were measured at four temperatures between 288.15 K and 318.15 K and in  $0 \leq x_2 \leq 0.10$  concentration range. The dynamic viscosities and densities of the mixtures diluted for the systems DMETEG + 2-PR, DMETEG + 2-BU were obtained from the reference [8].

### 4. Theoretical relations

Tamamushi and Isono [9] show that the dependence of the molar Gibbs energy of activation for viscous flow with the mole fraction for dilute solutions can be obtained from the empirical relation:

$$\Delta G_{1,2}^* = \Delta G_1^{0,*} + \beta_G x_2 + \gamma_G x_2^2 \quad (1)$$

where  $\Delta G_{1,2}^*$ , the average molar Gibbs energy of activation for viscous flow of the solution ( $\text{J}\cdot\text{mol}^{-1}$ ),  $\Delta G_1^{0,*}$  is the activation Gibb's energy for viscous flow for the pure solvent,  $\beta_G$  and  $\gamma_G$  are the empirical activation energetic parameters of viscous flow,  $x_2$  is the mole fraction of solute ( component 2).

The activation energetic parameter by viscous flow  $\beta_G$  is the difference between the partial molar activation parameter for viscous flow of the solute at infinite dilution and the corresponding partial molar property of the pure solvent ( $\Delta G_{2,0} - \Delta G_1^0$ ) when  $x_2 \rightarrow 0$  [10].

The relative viscosity of a dilute solution of non-electrolytes was calculated by

$$\eta_r = \frac{\eta_{1,2}}{\eta_1} = 1 + Bm + Dm^2 \quad (2)$$

where  $\eta_{1,2}$ ,  $\eta_1$  are the viscosity of the mixture and the pure solvent respectively,  $B$  is the interaction solute–solvent Jones–Dole' coefficient and also depend on the molecules' form and size,  $D$  is a interaction coefficient too [11] and  $m$  is the molality of mixture.

Taking into account the theory of Eyring's processes of velocity applied to the viscous flow, it is possible to obtain the relation between  $B$  and  $\beta_G$  [12].

$$\left( V_1^0 - \bar{V}_2^\infty \right) = \frac{1}{\rho_1} \left( B - \frac{\beta_G M_1}{RT} \right) \quad (3)$$

where  $V_1^0$  and  $\bar{V}_2^\infty$  represent the molar volume of the pure solvent and the partial molar volume of the solute at infinite dilution, respectively.  $\rho_1$  and  $M_1$  are the density and molar mass of pure solvent, respectively. According to Eq. (3), the  $\bar{V}_2^\infty$  can be obtained from calculating  $V_1^0$  of the solvent.

**Table 1**

The dynamic viscosities ( $\eta_{1,2}$ ) and the densities ( $\rho$ ) of the mixtures for the system TRIEGMME + 2-PR in function of concentration.

TRIEGMME + 2-PR					
$x_2$	m (mol·kg <sup>-1</sup> )	$\eta_{1,2}$ ( mPa·s)			
		288.15 K	298.15 K	308.15 K	318.15 K
0.0000	0.0000	2.847	2.089	1.562	1.193
0.0079	0.1325	2.835	2.089	1.568	1.202
0.0146	0.2465	2.827	2.090	1.574	1.210
0.0314	0.5394	2.824	2.099	1.594	1.235
0.0413	0.7168	2.826	2.116	1.608	1.252
0.0581	1.0264	2.840	2.128	1.628	1.266
0.0775	1.3979	2.871	2.159	1.683	1.300
0.1025	1.9004	2.922	2.207	1.706	1.343
$x_2$	m (mol·kg <sup>-1</sup> )	$\rho$ (kg·m <sup>-3</sup> )			
		288.15 K	298.15 K	308.15 K	318.15 K
0.0000	0.0000	789.1	780.9	772.5	763.5
0.0079	0.1325	793.3	785.1	776.6	767.7
0.0146	0.2465	796.9	788.7	780.2	771.3
0.0314	0.5394	805.9	797.3	788.8	779.9
0.0413	0.7168	811.0	802.5	794.0	785.0
0.0581	1.0264	819.1	810.8	802.1	793.0
0.0775	1.3979	828.0	819.6	811.1	802.3
0.1025	1.9004	839.6	831.2	822.6	813.7

The apparent molar volumes  $V_{\phi,2}$  of the solute were calculated by:

$$V_{\phi,2} = \left( \frac{M_2}{\rho} \right) - \left( \frac{\rho - \rho_1}{\rho^* \rho_1} \right) \frac{1000}{m} \quad (4)$$

where  $M_2$  is molar mass of solute,  $m$  is concentration of solute in molality (mol·kg<sup>-1</sup>),  $\rho$  and  $\rho_1$  are densities of solution and pure solvent, respectively. By extrapolating the apparent molar volume values at infinite dilution condition,  $\bar{V}_2^\infty$  can be obtained.

From the Terasawa's relation [5] it is possible to express the partial molar volume by means of the addition of a volume called of van der Waals volume ( $V_w$ ), by Bondi [6], and a volume referred to as empty or void volume,  $V_v$  :

$$\bar{V}_2^\infty = V_w + V_v \quad (5)$$

$V_w$  is the volume occupied by the molecule of solute, in other words, the volume impenetrable to the solvent molecules and the void

**Table 2**

The dynamic viscosities ( $\eta_{1,2}$ ) and the densities ( $\rho$ ) of the mixtures for the system TRIEGMME + 2-BU in function of concentration.

TRIEGMME + 2-BU					
$x_2$	m (mol·kg <sup>-1</sup> )	$\eta_{1,2}$ (mPa·s)			
		288.15 K	298.15 K	308.15 K	318.15 K
0.0000	0.0000	4.624	3.120	2.171	1.563
0.0039	0.0528	4.586	3.101	2.163	1.565
0.0079	0.1074	4.518	3.074	2.161	1.562
0.0151	0.2068	4.450	3.046	2.148	1.564
0.0318	0.4431	4.307	2.988	2.133	1.569
0.0511	0.7265	4.182	2.947	2.132	1.577
0.0800	1.1732	4.053	2.893	2.128	1.611
0.1038	1.5626	3.991	2.942	2.186	1.674
$x_2$	m (mol·kg <sup>-1</sup> )	$\rho$ (kg·m <sup>-3</sup> )			
		288.15 K	298.15 K	308.15 K	318.15 K
0.0000	0.0000	810.3	802.3	793.9	785.1
0.0039	0.0528	811.9	803.9	795.6	786.7
0.0079	0.1074	813.5	805.5	797.1	788.2
0.0151	0.2068	816.3	808.3	799.9	791.1
0.0318	0.4431	822.7	814.7	806.3	797.5
0.0511	0.7265	829.9	821.9	813.5	804.8
0.0800	1.1732	840.5	832.5	824.0	815.3
0.1038	1.5626	848.9	840.8	832.4	823.7

**Table 3**  
The dynamic viscosities ( $\eta_{1,2}$ ) and the densities ( $\rho$ ) of the mixtures for the system TRIEGMME + 2-PE in function of concentration.

TRIEGMME + 2-PE					
$x_2$	m (mol·kg <sup>-1</sup> )	$\eta_{1,2}$ (mPa·s)			
		288.15 K	298.15 K	308.15 K	318.15 K
0.0000	0.0000	5.093	3.380	2.330	1.674
0.0047	0.0536	5.022	3.349	2.319	1.672
0.0177	0.2044	4.894	3.306	2.316	1.676
0.0299	0.3497	4.778	3.258	2.300	1.684
0.0546	0.6552	4.608	3.191	2.288	1.695
0.0827	1.0228	4.459	3.143	2.285	1.712
0.1089	1.3864	4.383	3.122	2.295	1.732
$x_2$	m (mol·kg <sup>-1</sup> )	$\rho$ (kg·m <sup>-3</sup> )			
		288.15 K	298.15 K	308.15 K	318.15 K
0.0000	0.0000	812.8	804.7	796.6	788.1
0.0047	0.0536	814.2	806.4	798.2	789.6
0.0177	0.2044	818.7	810.8	802.7	793.9
0.0299	0.3497	822.5	814.5	806.4	797.8
0.0546	0.6552	830.3	822.4	814.3	805.7
0.0827	1.0228	839.1	831.2	823.0	814.5
0.1089	1.3864	847.0	839.1	831.0	822.4

volume ( $V_v$ ) can be considered as the volume of the dead space generated by the addition of one mole of solute to the solvent.

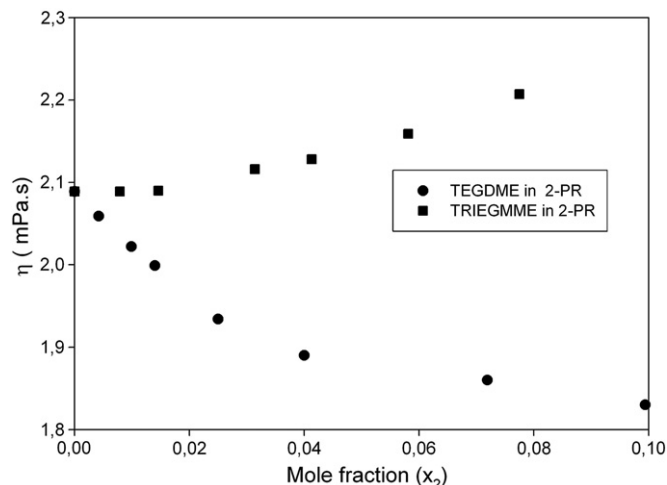
### 5. Results and discussion

The dynamic viscosities ( $\eta$ ) and the densities ( $\rho$ ) values of the dilute solution for the systems TRIEGMME + 2-PR, TRIEGMME + 2-BU and TRIEGMME + 2-PE are included in Tables 1, 2, and 3, respectively. The densities and dynamic viscosities values of the systems TEGDME + 2-PE at the working temperatures are shown in Table 4. The dynamic viscosities and densities values of the mixtures diluted for the TEGDME + 2-PR and TEGDME + 2-BU systems were obtained from the reference [8].

Figs. 1, 2, and 3 show the dynamic viscosity values of the TRIEGMME and TEGDME solutes in 2-PR, 2-BU, and 2-PE at 298.15 K. All the systems have less viscosity than the solvent except the TRIEGMME + 2-PR system. It is possible that the TRIEGMME as

**Table 4**  
The dynamic viscosities ( $\eta_{1,2}$ ) and the densities ( $\rho$ ) of the mixtures for the system TEGDME + 2-PE in function of concentration.

TEGDME + 2-PE					
$x_2$	m (mol·kg <sup>-1</sup> )	$\eta_{1,2}$ (mPa·s)			
		288.15 K	298.15 K	308.15 K	318.15 K
0.0000	0.0000	5.093	3.380	2.330	1.674
0.0055	0.0627	4.940	3.301	2.291	1.658
0.0094	0.1076	4.856	3.260	2.274	1.638
0.0147	0.1693	4.742	3.223	2.250	1.631
0.0256	0.2980	4.433	3.071	2.203	1.622
0.0397	0.4690	4.150	2.910	2.117	1.575
0.0606	0.7318	3.864	2.750	2.046	1.533
0.0791	0.9744	3.653	2.641	1.977	1.524
0.0929	1.1618	3.541	2.580	1.940	1.497
0.1008	1.2717	3.480	2.550	1.910	1.480
$x_2$	m (mol·kg <sup>-1</sup> )	$\rho$ (kg·m <sup>-3</sup> )			
		288.15 K	298.15 K	308.15 K	318.15 K
0.0000	0.0000	812.8	804.7	796.6	788.1
0.0055	0.0627	814.8	806.9	798.6	790.1
0.0094	0.1076	817.0	808.6	800.3	791.7
0.0147	0.1693	818.5	810.5	802.2	793.8
0.0256	0.2980	822.6	814.7	806.4	797.8
0.0397	0.4690	827.8	819.8	811.6	803.0
0.0606	0.7318	835.1	826.9	818.7	810.3
0.0791	0.9744	841.3	833.3	825.0	816.5
0.0929	1.1618	846.1	837.9	829.6	821.1
0.1008	1.2717	849.2	841.1	832.7	824.2



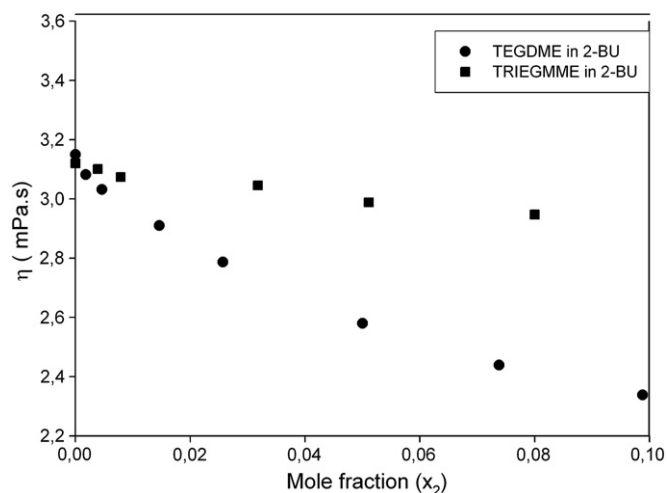
**Fig. 1.** The experimental dynamic viscosity ( $\eta$ ) against mole fraction ( $x_2$ ) at 298.15 K: (■), TRIEGMME in 2-PR; (●), TEGDME in 2-PR.

solute acting as maker of the solvent structure by hydrogen bonding formation between solute–solvent and then the viscosity of solutions is higher than that the solvent [13]. A similar behavior has been observed for the 1-propanol (1-PR) and 1-butanol (1-BU) in polyethylene glycol 350 mono methyl ether PEGMME [14,15].

The Jones–Dole B coefficients and  $\beta_G$  parameters for viscous flow are included in Table 5 with the respective error values at a level of 95%. The greater errors values correspond to TEGDME + 2-PR and TEGDME + 2-BU systems calculated of the reference [8].

The values of Jones–Dole coefficients are negative for all systems except in the case of TRIEGMME + 2-PR according to obtained dynamic viscosity values and lightly increase with the temperature. Positive values for Jones–Dole B coefficients have been found in the PEGMME with 1-PR and 1-BU [15].

The  $\beta_G$  parameters for viscous flow represents the difference between the solute partial molar Gibbs energy of activation for viscous flow at infinite dilution and the partial molar Gibbs energy of activation for viscous flow of the pure solvent [10]. In Table 5, the  $\beta_G$  parameters for viscous flow values for the TRIEGMME + 2-PR systems are positive and increase with the temperature. The values for TRIEGMME with 2-BU and 2-PE are negative except the last values in both systems. In the TEGDME with 2-PR, 2-BU, and 2-PE systems the



**Fig. 2.** The experimental dynamic viscosity ( $\eta$ ) against mole fraction ( $x_2$ ) at 298.15 K: (■), TRIEGMME in 2-BU; (●), TEGDME in 2-BU.

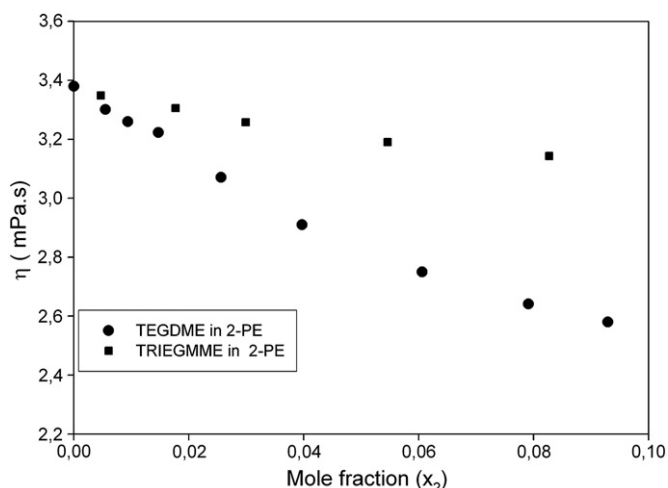


Fig. 3. The experimental dynamic viscosity ( $\eta$ ) against mole fraction ( $x_2$ ) at 298.15 K: (■), TRIEGMME in 2-PE; (●), TEGDME in 2-PE.

$\beta_G$  parameters values are negative except the two last values in the TEGDME + 2-PR systems. When the difference between solute partial molar Gibbs energy of activation for viscous flow at infinite dilution and the partial molar Gibbs energy of the pure solvent are positive we could say that the solute–solvent bonds are stronger than the solvent–solvent as can be observed by the TRIEGMME + 2-PR systems. A similar behavior in TRIEGMME + 2-PR systems is found when polyethylene glycol 350 monomethyl ether is used as solute in 1-propanol (1-PR) and 1-butanol (1-BU) [15]. In the PEGMME + 1-PR and PEGMME + 1-BU systems the  $\beta_G$  parameters for viscous flow values are positive too and we can conclude that solute–solvent bonds are stronger than solvent–solvent bonds.

In Table 6 we have included at all work temperatures for both solutes in 2-PR, the solvent molar volume values, the volumetric difference values of the first term of Eq. (3), and the values of the relation between the partial molar volumes at infinite dilution obtained from viscosity data and the partial molar volume at infinite dilution obtained from density data. The same property values that can be seen in Table 6 have been included for the solvents 2-BU and 2-PE.

In Table 6 we found that the only systems in which deviations are minor to 5% between the values obtained by viscosimetric via with the values obtained through volumetric measurements are the

Table 5 The coefficient of Jones–Dole B ( $\text{kg}\cdot\text{mol}^{-1}$ ) and the activation energetic parameter by viscous flow  $\beta_G$  ( $\text{kJ}\cdot\text{mol}^{-1}$ ) at different temperatures.

T	TRIEGMME + 2-PR		TRIEGMME + 2-BU		TRIEGMME + 2-PE	
	$B\cdot 10^3 \pm \sigma$	$\beta_G \pm \sigma$	$B\cdot 10^3 \pm \sigma$	$\beta_G \pm \sigma$	$B\cdot 10^3 \pm \sigma$	$\beta_G \pm \sigma$
288.15	$-24 \pm 2$	$1.2 \pm 0.1$	$-190 \pm 40$	$-4.2 \pm 0.2$	$-220 \pm 6$	$-4.3 \pm 0.1$
298.15	$0 \pm 4$	$2.5 \pm 0.2$	$-127 \pm 20$	$-2.2 \pm 0.4$	$-140 \pm 20$	$-2.3 \pm 0.1$
308.15	$25 \pm 2$	$3.9 \pm 0.4$	$-69 \pm 15$	$-0.2 \pm 0.1$	$-80 \pm 9$	$-0.3 \pm 0.1$
318.15	$50 \pm 9$	$5.2 \pm 0.4$	$-15 \pm 6$	$1.8 \pm 0.3$	$-15 \pm 6$	$1.8 \pm 0.1$
T	TEGDME + 2-PR		TEGDME + 2-BU		TEGDME + 2-PE	
	$B\cdot 10^3 \pm \sigma$	$\beta_G \pm \sigma$	$B\cdot 10^3 \pm \sigma$	$\beta_G \pm \sigma$	$B\cdot 10^3 \pm \sigma$	$\beta_G \pm \sigma$
288.15	$-290 \pm 200$	$-5.3 \pm 0.8$	$-690 \pm 450$	$-11.9 \pm 2.2$	$-690 \pm 10$	$-10.2 \pm 0.4$
298.15	$-220 \pm 200$	$-1.7 \pm 0.9$	$-590 \pm 400$	$-8.5 \pm 2.1$	$-600 \pm 20$	$-7.1 \pm 0.3$
308.15	$-160 \pm 100$	$1.4 \pm 0.8$	$-470 \pm 280$	$-4.3 \pm 1.9$	$-500 \pm 20$	$-4.0 \pm 0.2$
318.15	$-120 \pm 70$	$3.6 \pm 0.8$	$-420 \pm 250$	$-1.1 \pm 0.7$	$-440 \pm 10$	$-1.0 \pm 0.2$

Table 6 The molar volume of pure solvent ( $V_1^0$ ), values of the volumetric difference in equation (3) ( $V_1^0 - V_2^{\infty,v}$ ), and the relations between partial molar volumes at infinite dilution calculated at different temperatures.

T (K)	$V_1^0$	$(V_1^0 - V_2^{\infty,v})$	$(V_2^{\infty,v} / V_2^{\infty,p})$	$(V_1^0 - V_2^{\infty,v})$	$(V_2^{\infty,v} / V_2^{\infty,p})$
TRIEGMME + 2-PR					
288.15	76.16	-68.88	0.928	-199.04	1.268
298.15	76.96	-78.85	0.990	-228.95	1.399
308.15	77.79	-84.83	1.019	-249.63	1.487
318.15	78.71	-88.94	1.051	-264.29	1.548
TRIEGMME + 2-BU					
288.15	91.48	-74.13	1.059	-397.59	2.246
298.15	92.39	-76.68	1.074	-418.62	2.331
308.15	93.36	-80.35	1.095	-434.07	2.386
318.15	94.41	-84.42	1.119	-495.71	2.650
TRIEGMME + 2-PE					
288.15	108.45	-75.13	1.173	-387.22	2.254
298.15	109.54	-82.73	1.224	-431.01	2.444
308.15	110.66	-88.77	1.261	-452.76	2.521
318.15	111.85	-93.45	1.285	-517.29	2.796

TRIEGMME + 2-PR. In general the deviations in the systems that contain TRIEGMME as a solute are minor than in the systems with TEGDME. The deviations increment with temperature in all systems.

The analysis of the results leads us to conclude that although the values obtained using viscosity data and the relations obtained through Klotz [12] show values with high deviation in relation to the ones obtained by volumetric via, which leads us to think that these deviations could be related to solute structure in these solvents.

The polyalkyl glycol ether molecules can interact with 2-alkanols through the hydroxyl groups via formation of hydrogen bonds, which would produce a volume contraction which would mean a minor partial molar volume of the solute. In these systems there could exist three types of H-bonds: intramolecular H-bond, OH–OH intermolecular and OH–O intermolecular. It is well known that the alcohol–alcohol bonds are stronger than the alcohol–ether ones [16], thus at low polyalkyl glycol ether concentrations the alcohol–alcohol can be more important than the alcohol–ether.

The TRIEGMME has intermolecular and intramolecular H-bonding possibilities, different from the TEGDME which presents only intermolecular possibilities. Therefore, in the TRIEGMME + 2-alkanols systems there coexist solute–solvent interactions through intermolecular hydrogen bonds and the possibility of formation of intramolecular H-bonds which would mean a certain degree of cyclic compound [17].

When we analyze the differences between the partial molar volume at infinite dilution obtained from volumetric data and the molar volume of TRIEGMME obtained from the density values of the pure component, they are small and negative and they show a tendency to diminish and be positive in the TEGDME as it goes from 2-propanol to 2-pentanol. This could only indicate a volume expansion in the latter systems.

A possible explanation of the behavior in these systems are the formation of H-bond, and those the steric effects and the temperature on the H-bonds, which can be seen in the difference of behavior between 1-alkanols and 2-alkanols [18], and the effect of the increase in the hydrocarbon chain is mayor as it goes from 2-propanol to a 2-BU and a 2-PE.

The values of the viscosimetric properties found in the systems that contain TRIEGMME could be explained from this point of view. However, this could not explain the mayor viscosity of the solution when it is compared with the pure solvent that we find in the TRIEGMME + 2-PR system.

The void volume values obtained for the all study systems by using the Eq. (5) are showed in Fig. 4. The van der Waals volume values for both solutes have been obtained through the Lepori and Gianini

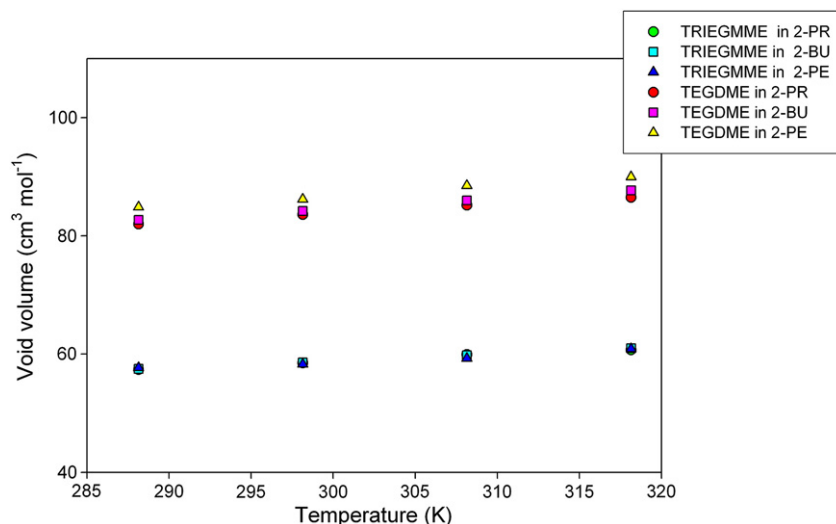


Fig. 4. Void volume,  $V_v$ , of the solutes in 2-alkanols against temperature: (●), 2-propanol; (■), 2-butanol; (▲), 2-pentanol.

method [7]. The greater values of void volume obtained in the TEGDME + 2-alkanols could explain the incidence of the effects of hydrogen bonds in the greater fluidity of the mixtures containing tetraethylene glycol dimethyl ether.

As a way of comparing compounds with differences in the hydrocarbon chains like the systems that have been studied in this work, we have used the void reduced volume obtained through the Terasawa model [5]. The void reduced volume is obtained through:

$$\bar{V}_e = \frac{V_v}{V_w} \quad (6)$$

In Fig. 5 we have included the values obtained for both solutes in 2-alkanols.

It can be observed that the void reduced volume values ( $\bar{V}_e$ ) that correspond to TRIEGMME in the three alcohols are lower than the values that correspond to TEGDME in these solvents as could be expected in this type of system. The void reduced values ( $\bar{V}_e$ ) of TEGDME show a slight increase as it goes from 2-propanol to 2-pentanol, different from what occurs in TRIEGMME which does not show changes in any of the three solvents, which could confirm the volumetric expansion as it goes from 2-propanol to 2-pentanol.

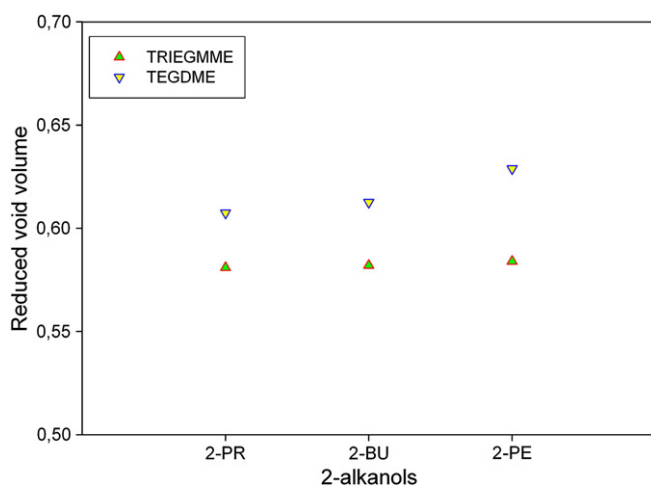


Fig. 5. Reduced void volume,  $\bar{V}_e$ , of the TRIEGMME and TEGDME at 298.15 K.

## 6. Conclusion

The Jones–Dole B coefficients and  $\beta_G$  parameters for viscous flow values were calculated and explain the viscosimetric behavior of the two polyalkyl glycol ethers in 2-alkanols. The TRIEGMME + 2-PR system shows greater viscosity values than the pure solvent. The positive values for Jones–Dole (B) coefficients and the interaction parameters for viscous flow ( $\beta_G$ ) obtained show that solute–solvent bonds are stronger than solvent–solvent bonds and they are coherent with viscosimetric behavior in this system. The formation of intramolecular H-bond could be responsible for the different dynamic viscosity values in this system.

The relation between the Jones Dole's B coefficient and the  $\beta_G$  parameter of viscous flow obtained from viscosity measured has allowed us to calculate the volumetric component in the equation of Klotfutar [10,12]. The values obtained for partial molar volume at infinite dilution were compared with the ones obtained through density measures. The major deviations can be observed when the TEGDME is used as solute in the three 2-alkanols. The deviations are analyzed in terms of the behavior of both solutes in 2-alkanols. The differences between the molar volume of the pure solutes and the partial molar volume obtained through density measurements show a volume expansion in TEGDME which increases as it goes from 2-propanol to 2-pentanol. The values of dead volume and dead reduced volume by Terasawa relation [5] confirm the latter estimation. The differences between TRIEGMME and TEGDME in 2-alkanols are explained by volumetric properties calculated. However, these properties cannot explain the viscosimetric behavior found in the TRIEGMME + 2-PR system.

## Acknowledgements

The present work was financed by a CIUNT research grant. E. L. A. is a member of the CONICET.

## References

- [1] S. Aznarez, M.F. de Ruiz Holgado, E.L. Arancibia, J. Mol. Liquids 124 (2006) 78.
- [2] S. Aznarez, M.F. de Ruiz Holgado, E.L. Arancibia, J. Mol. Liquids 139 (2008) 131.
- [3] A. Coronas, M. Vallrs, S.K. Chaudhari, K.R. Patil, Appl. Therm. Eng. 4 (1996) 335.
- [4] M.J.P. Camuñas, A. Baylaucq, F. Plantier, C. Poned, J. Fernandez, Fluid Phase Equilib. 331 (2004) 222.
- [5] S. Terasawa, H. Itsuki, S. Arakawa, J. Phys. Chem. 79 (1975) 2345.
- [6] A. Bondi, J. Phys. Chem. 68 (1964) 441.
- [7] L. Lepori, P. Gianni, J. Solut. Chem. 29 (2000) 405.

- [8] S. Aznarez, A. Amid, M.M.E.F. de Ruiz Holgado, E.L. Arancibia, *J. Mol. Liquids* 115 (2004) 69.
- [9] R. Tamamushi, T. Isono, *J. Chem. Soc. Faraday Trans. 1* 80 (1984) 2751.
- [10] C. Koflutar, S. Paljk, M. Kac, *Thermochim. Acta* 153 (1989) 297.
- [11] T.T. Herskovits, T.M. Kelly, *J. Phys. Chem.* 77 (1973) 381.
- [12] C. Koflutar, S. Paljk, S. Golc-Tejer, *Thermochim. Acta* 206 (1992) 19.
- [13] D. Feakins, W.E. Waghorne, K.G. Lawrence, *J. Chem. Soc. Faraday Trans. 1* 82 (1986) 563.
- [14] M.M.E.F. de Ruiz Holgado, C.R. de Schaefer, E.L. Arancibia, *J. Mol. Liquids* 79 (1999) 257.
- [15] M.M.E.F. de Ruiz Holgado, C.R. de Schaefer, E.L. Arancibia, *Fluid Phase Equilib.* 169 (2000) 237.
- [16] R.B. Gupta, R.L. Brinkley, *AIChE J.* 44 (1998) 207.
- [17] R.L. Brinkley, R.B. Gupta, *Ind. Eng. Chem. Res.* 37 (1998) 4823.
- [18] L. Sun, C.D. Wick, J.I. Siepmann, M.R. Schure, *J. Phys. Chem. B* 109 (2005) 15118.