



## VISCOSITY AND DENSITY OF SYSTEMS WITH WATER, 1,4-DIOXANE AND ETHYLENE GLYCOL BETWEEN (293.15 AND 313.15) K. I. BINARY SYSTEMS

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The kinematic viscosities and densities of the binary liquid mixtures: water+ethylene glycol, 1,4-dioxane +ethylene glycol and water+1,4-dioxane were measured between 293.15 and 313.15 K over the whole range of the mixture compositions. The viscosity deviations ( $\Delta\nu$ ), excess molar volumes ( $V^E$ ) and excess Gibbs energy of activation of viscous flow ( $G^{*E}$ ) were calculated from experimental data; all the computed quantities have been fitted to the Redlich-Kister equation. Also, the partial excess molar volumes ( $\bar{V}_i^E$ ) were calculated from the smoothed data excess functions for the investigated systems. The results are discussed and interpreted in terms of molecular package and specific interaction predominated by hydrogen bonding.

### INTRODUCTION

Continuing our work on the thermodynamic of the systems with glycols<sup>1-3</sup> this paper presents a part of a series of investigations on physico-chemical properties (density and viscosity) of the binary systems containing water, 1,4-dioxane and ethylene glycol.

Data referring to the properties of pure substances or mixtures are required for the optimal design of industrial chemical equipments. The studied systems have industrial utility; the water + organic type solvents are frequently used as chemical and biochemical reaction media.

The study of physico-chemical properties of systems with glycols and water is important for understanding the influence of the intermolecular interactions between water and the compounds containing hydroxylic groups, the glycols having both hydrophilic and hydrophobic groups. Ethylene glycol, the simplest glycol, and its mixtures are models for the study of more complex chemical and biochemical systems, from interactional point of view. The mixtures of unassociated and non-aprotic solvents such as 1,4-

dioxane, or slightly associated solvents, present theoretical and practical interest. The study of solutions properties with non-polar or slight polar molecules represents the key of the understanding of the non-electrolyte solutions behavior.

This paper reports the results of our experimental study on the viscosity and density of the binary systems water+ethylene glycol (EG), 1,4-dioxane+ethylene glycol and water+1,4-dioxane at five temperatures ranging from 293.15 to 313.15 K. The main objectives of this paper are to report new experimental density data for water+ethylene glycol (EG) and 1,4-dioxane+ethylene glycol systems and to calculate the viscosity deviations, excess molar volumes, excess Gibbs energy of activation of viscous flow ( $G^{*E}$ ) and the partial excess molar volumes ( $\bar{V}_i^E$ ) for all investigated binary systems. The experimental excess functions were fitted to the Redlich-Kister type polynomial equation. The densities and excess molar volumes for the water+1,4-dioxane system were previously reported<sup>4</sup>. The study of these binary mixtures is a necessary step in analyzing and discussing the corresponding ternary system into a future work.

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To our knowledge, a literature study shows that information regarding viscometric and volumetric properties is limited for the 1,4-dioxane +ethylene glycol system,<sup>5,6</sup> the other two systems being reported quite frequently in literature.<sup>7-10</sup>

## EXPERIMENTAL

**Materials.** The analytical-reagent-grade 1,4-dioxane from Merck was distilled at 374.15K to collect the middle fractions; the water was distilled twice and the analytical-reagent-grade ethylene glycol from Merck p.a. was used without further purification. The purity of the materials was checked by the means of gas chromatographic analysis. It was better than 99.5 mass%. The comparison between literature values and the pure component values of the density and *dynamic viscosity* measured in this work is presented in Table 1.

**Apparatus and procedure.** The kinematic viscosities and the densities of the pure liquids and of their mixtures were

experimentally measured for the entire range of the composition. The kinematic viscosity ( $\nu$ ) was measured using an Ubbelohde viscometer, and the density ( $\rho$ ) by conventional pycnometric method having a bulb volume of 25 cm<sup>3</sup> and a capillary with an internal diameter of 1 mm. The weighings were done with a HR-120 (A&D Japan) balance with a precision of 0.0001 g. An average of triplicate measurements was considered and this was accurate to  $\pm 0.0002$  g·cm<sup>-3</sup>. The dynamic viscosity ( $\eta$ ) was calculated using the relation:  $\eta = \nu \cdot \rho$ .

The viscometer was calibrated using triple-distilled water and pure solvents. The time of fall always exceeded 60 seconds; the accuracy of the measurement of the time was 0.1 seconds. Consequently, the errors of the measured values of the viscosity may be estimated as low as 1%. A thermostatically controlled bath was used to keep the temperature within  $\pm 0.05$  K. The mixtures were prepared volumetrically. The accuracy of the mole fraction was estimated at  $\pm 0.002$ . All mixtures were completely miscible over the whole composition range.

Table 1

Comparison between measured and literature data for kinematic viscosities ( $\nu$ ) and densities ( $\rho$ ) of pure components at 298.15 K

Component	$\nu$ , mm <sup>2</sup> ·s <sup>-1</sup>		$\rho$ , g·cm <sup>-3</sup>	
	Exp.	Lit.	Exp.	Lit.
water	0.9191	0.8934 <sup>9</sup>	0.9973	0.99712 <sup>12</sup>
		0.895 <sup>11</sup>		0.99720 <sup>7</sup>
		0.9498 <sup>7</sup>		0.9973 <sup>9</sup>
1,4-dioxane	1.1578	1.1347 <sup>5</sup>	1.0280	1.0276 <sup>5</sup> 1.0280 <sup>13</sup>
ethylene glycol	15.2515	13.3514 <sup>14</sup>	1.1126	1.109913 <sup>15</sup>
		16.8388 <sup>7</sup>		1.1100 <sup>12</sup>
				1.1113 <sup>5</sup>

## RESULTS AND DISCUSSION

The experimental data of kinematic viscosities ( $\nu$ ) and densities ( $\rho$ ) for the binary systems of ethylene glycol with water and 1,4-dioxane at 293.15, 298.15, 303.15, 308.15 and 313.15 K are presented in Table 2.

From the experimental data, derived quantities: viscosity deviations ( $\Delta\nu$ ) and excess molar volumes ( $V^E$ ) were calculated by means of the Eqs. (1)-(2).

$$\Delta\nu = \nu - \sum_{i=1}^2 \nu_i X_i \quad (1)$$

$$V^E = \sum_{i=1}^2 X_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (2)$$

where  $X_i$  is the mole fraction of component  $i$ ,  $\rho$  and  $\nu$  are the density and kinematic viscosity of the

binary mixture, respectively,  $M_i$ ,  $\rho_i$ ,  $\nu_i$  are the molar mass, density and kinematic viscosity of the pure components, respectively.

From the measured viscosities and densities the excess Gibbs energies of activation of viscous flow ( $G^{*E}$ ) were calculated on the basis of the theory of absolute reaction rate with the Eq. (3).

$$G^{*E} = RT \left[ \ln(V\eta) - \sum_{i=1}^N X_i \ln(V_i \eta_i) \right] \quad (3)$$

where  $V$  and  $\eta$  are the molar volume and dynamic viscosity of the binary mixture, respectively;  $V_i$  and  $\eta_i$  are the molar volume and dynamic viscosity of the pure components, respectively.  $R$  is the gas constant and  $T$  the absolute temperature.

Table 2

Kinematic viscosities and densities for binary systems water (1)+EG (2) and 1,4-dioxane (1)+EG(2) at different temperatures

$X_1$	$\nu$ $\text{mm}^2\cdot\text{s}^{-1}$	$\rho$ $\text{g}\cdot\text{cm}^{-3}$	$X_1$	$\nu$ $\text{mm}^2\cdot\text{s}^{-1}$	$\rho$ $\text{g}\cdot\text{cm}^{-3}$
<b>water (1)+EG(2)</b>					
<b>T=293.15 K</b>					
0.0000	19.0677	1.1140	0.5984	6.2890	1.0886
0.0941	16.7623	1.1128	0.7039	4.5818	1.0770
0.2006	14.3224	1.1100	0.8072	3.1160	1.0601
0.2452	13.2552	1.1087	0.8992	2.0043	1.0372
0.3963	10.1206	1.1025	1.0000	1.0050	0.9982
0.5010	8.0990	1.0963			
<b>T=298.15 K</b>					
0.0000	15.2515	1.1126	0.5984	5.2865	1.0871
0.0941	13.5800	1.1107	0.7039	4.1554	1.0757
0.2006	11.6218	1.1080	0.8072	2.6923	1.0592
0.2452	10.9539	1.1066	0.8992	1.7407	1.0367
0.3963	8.4555	1.1006	1.0000	0.9191	0.9973
0.5010	6.7475	1.0947			
<b>T=303.15 K</b>					
0.0000	12.4479	1.1104	0.5984	4.4610	1.0859
0.0941	11.1626	1.1093	0.7039	3.3103	1.0746
0.2006	9.7025	1.1066	0.8072	2.3103	1.0582
0.2452	9.0748	1.1052	0.8992	1.5119	1.0358
0.3963	7.0259	1.0992	1.0000	0.8042	0.9956
0.5010	5.6616	1.0933			
<b>T=308.15 K</b>					
0.0000	10.5432	1.1082	0.5984	3.7955	1.0846
0.0941	9.2405	1.1077	0.7039	2.8463	1.0734
0.2006	8.0770	1.1052	0.8072	2.0373	1.0573
0.2452	7.4800	1.1037	0.8992	1.3657	1.0350
0.3963	5.9495	1.0978	1.0000	0.7232	0.9940
0.5010	4.7565	1.0919			
<b>T=313.15 K</b>					
0.0000	8.6793	1.1068	0.5984	3.3143	1.0835
0.0941	7.7969	1.1063	0.7039	2.5843	1.0723
0.2006	6.6957	1.1037	0.8072	1.7804	1.0562
0.2452	6.3634	1.1024	0.8992	1.2367	1.0337
0.3963	5.0638	1.0965	1.0000	0.6611	0.9922
0.5010	4.1497	1.0908			
<b>1,4-dioxane (1)+EG(2)</b>					
<b>T=293.15 K</b>					
0.0000	19.0677	1.1140	0.6012	2.1813	1.0621
0.0998	13.3070	1.1044	0.7017	1.9201	1.0550
0.1987	8.5570	1.0948	0.8006	1.6978	1.0481
0.2991	5.5320	1.0857	0.9003	1.4807	1.0411
0.3977	3.7092	1.0775	1.0000	1.2694	1.0339
0.4977	2.7354	1.0697			
<b>T=298.15 K</b>					
0.0000	15.2515	1.1126	0.6012	2.0298	1.0576
0.0998	11.0930	1.1018	0.7017	1.7910	1.0501
0.1987	7.6240	1.0918	0.8006	1.5712	1.0429
0.2991	5.1909	1.0823	0.9003	1.4165	1.0355
0.3977	3.5032	1.0737	1.0000	1.1578	1.0280
0.4977	2.5786	1.0655			
<b>T=303.15 K</b>					
0.0000	12.4479	1.1104	0.6012	1.8402	1.0535
0.0998	9.1550	1.1000	0.7017	1.4594	1.0457
0.1987	6.7025	1.0895	0.8006	1.4323	1.0381
0.2991	4.9173	1.0795	0.9003	1.3488	1.0304
0.3977	3.2945	1.0705	1.0000	1.0882	1.0225
0.4977	2.2631	1.0619			

Table 2 (continued)

T=308.15 K					
0.0000	10.5432	1.1082	0.6012	1.7467	1.0495
0.0998	7.8111	1.0980	0.7017	1.4591	1.0414
0.1987	5.8490	1.0871	0.8006	1.2887	1.0335
0.2991	4.3560	1.0768	0.9003	1.2807	1.0255
0.3977	3.0322	1.0673	1.0000	1.0182	1.0172
0.4977	2.1826	1.0583			
T=313.15 K					
0.0000	8.6793	1.1068	0.6012	1.6546	1.0457
0.0998	6.5824	1.0963	0.7017	1.4587	1.0372
0.1987	4.9841	1.0850	0.8006	1.2219	1.0290
0.2991	3.7771	1.0741	0.9003	1.0597	1.0207
0.3977	2.8919	1.0642	1.0000	0.9488	1.0121
0.4977	2.1217	1.0548			

The experimental values of  $\Delta v$ ,  $V^E$  and  $G^{*E}$  were fitted to the Redlich-Kister type polynomials:

$$Y^E = X_i X_j \sum_{k=0}^p A_k (X_j - X_i)^k \quad (4)$$

where  $Y^E$  is the excess property and  $p$  is the degree of polynomial expansion. The adjustable parameters  $A_k$  obtained by fitting the equations to the experimental values with a least-squares algorithm are given in Table 3, along with the standard deviation,  $\sigma$ , defined as follows:

$$\sigma = \left[ \frac{\sum_{i=1}^n (Y_i^{\text{exp}} - Y_i^{\text{calc}})^2}{n - m} \right]^{0.5} \quad (5)$$

where  $n$  is the number of experimental data and  $m$  is the number of parameters.

The excess partial molar volumes of the components ( $\bar{V}_1^E$ ,  $\bar{V}_2^E$ ) were calculated from the following relationships:

$$\bar{V}_1^E = \bar{V}_1 - V_1 = V + X_2 \left( \frac{dV}{dX_1} \right) - V_1 \quad (6)$$

$$\bar{V}_2^E = \bar{V}_2 - V_2 = V - X_1 \left( \frac{dV}{dX_1} \right) - V_2 \quad (7)$$

The Figs. 1-9 present the experimental and calculated excess functions for the investigated binary systems at temperatures between 293.15 and 313.15 K.

The variation of  $\Delta\eta$  versus composition ( $X_1$ ) displayed in Figs. 1a, 4a and 7a show negative values for water + EG and 1,4-dioxane + EG systems, more accentuated for the last system and

positive deviations for water +1,4-dioxane system. The viscosity deviations ( $\Delta\eta$ ) has the order: water +1,4-dioxane > water + EG > 1,4-dioxane + EG.

Inspection of the results of Figs. 2, 5 and 8 indicates that the excess molar volumes are important negative for all studied systems, the biggest deviations being for water +1,4-dioxane system. The extent of negative variation of  $V^E$  for the systems has the sequence: water +1,4-dioxane > water + EG > 1,4-dioxane + EG.

In the Figs. 3, 6 and 9 are presented the excess partial molar volumes ( $\bar{V}_i^E$ ) vs composition. For all investigated systems, the partial excess molar volumes are negative for both components; their values gradually increase with the mole fraction of the respective component in the mixture. It can be observed an accentuated difference between the infinite dilution values for partial excess molar volumes of the components in the aqueous systems.

In the Figs. 1b, 4b and 7b are presented the calculated values for the excess Gibbs energies of activation of viscous flow ( $G^{*E}$ ) for the binary investigated systems, with positive values for the systems containing water and negative values for 1,4-dioxane + EG system.

The magnitude and sign of the given thermodynamic excess functions has contributions from various effects, interactional or structural. Generally, negative deviation of  $V^E$  and positive values for  $\Delta\eta$  suggests the presence of specific interactions between the components and geometrical accommodation of molecules on mixing and positive deviations of  $V^E$  and negative values for  $\Delta\eta$  are determined by weak intermolecular interactions and an advanced degree of unpacking/steric hindrance of the molecules in the mixture.

The liquids studied here differ from one another by molecular size, geometry, dipole moment, ability to form dipole–dipole bonds and hydrogen associations. Therefore, water is an interesting polar protic solvent ( $\mu = 1.85$  D) with small size, which is able to support extensive hydrogen-bonding networks. The ethylene glycol can also associate by hydrogen bonding; it has high dipole moment ( $\mu = 2.41$  D). 1,4-Dioxane ( $\mu = 0.4$  D) is a nonpolar aprotic solvent, but is able to associate by hydrogen bonding, due to its etheric oxygen.

Between water and ethylene glycol molecules are possible associations by hydrogen bonding and dipole–dipole interactions, which lead to negative excess volume. Since the molar volumes of water ( $18.0154 \text{ cm}^3\cdot\text{mol}^{-1}$ ) and ethylene glycol ( $62.0692 \text{ cm}^3\cdot\text{mol}^{-1}$ ) at 298.15 K differ considerably, it is possible that the small water molecules intercalate between the ethylene glycol molecules, which lead also to negative excess volume. Therefore, for the water + ethylene glycol system the main factors which affect the excess volumes are the hydrogen bonding and the molecular sizes and shapes of the molecules. For this system FTIR spectroscopy and UV-Vis spectroscopy studies illustrate the hydrogen bonding interactions of water with EG, being very successful methods to probe the molecular structure of association effects among molecules.<sup>16</sup>

Also, the  $V^E$  values are in accordance with negative values for  $H^E$ , with a minimum about  $-750 \text{ J mol}^{-1}$  at  $X_{\text{water}} \approx 0.65$  and 298.15 K.<sup>17</sup> Because in the water + EG system, the strength of interaction decreases in the sequence water-water > water-EG > EG-EG,<sup>8</sup> it seems that the interactions in the mixture are not so important as in pure components to give positive values for  $\Delta\eta$ , therefore viscosity deviation remain negative.

The  $V^E$  values increase in absolute values with increasing temperature and  $\Delta\eta$  has an opposite trend.

The  $V^E$  values at 293.15 K compare well with the reported results of Tsierkezos and Molinou<sup>7</sup> and Yang *et al.*<sup>8</sup> as is reflected in Fig. 2.

The 1,4-dioxane + ethylene glycol system is a mixture between a nonpolar aprotic solvent and a polar associated solvent, with a similar behavior concerning the sign of  $V^E$  and  $\Delta\eta$  as for the system water +EG. The more pronounced negative values for viscosity deviation of the 1,4-dioxane +EG system could be due to the weaker intermolecular interactions between 1,4-dioxane and EG molecules than between water and EG molecules. Because of that, the  $V^E$  values in the 1,4-dioxane +EG system are less negative than in the water +EG system. Nevertheless, dielectric studies in

literature have confirmed that although 1,4-dioxane has weak polar behavior, dielectric properties of 1,4-dioxane+ ethylene glycol system confirm the formation of stable adducts at the stoichiometric ratio 2:1 of ethylene glycol to 1,4-dioxane mole fraction.<sup>18</sup>

The  $V^E$  values increase in absolute values with increasing temperature and  $\Delta\eta$  has an opposite trend, as for the system with water.

The  $V^E$  values at 298.15 K compare well with the reported results of Nayak *et al.*<sup>5</sup> as is reflected in Fig. 5.

Unlike the above two systems, the water + 1,4-dioxane system presents a normal behavior concerning the sign of  $V^E$  and  $\Delta v$ : it has negative  $V^E$  values and positive  $\Delta\eta$  values.

The water + 1,4-dioxane system has a complex structure; the behavior of this system was discussed in detail into a previous paper<sup>4</sup>. The X ray diffraction, mass spectroscopy and NMR measurements show that on entire domain of concentration, the mixture presents (as function of concentration) the hydrogen bonded clusters characteristic to pure water (ice-like structure), hydrogen-bonded clusters of 1,4- dioxane and water molecules and structure of pure 1,4-dioxane, respectively. The water molecules forms hydrogen bonds with pure 1,4-dioxane clusters without altering its bulk structure.<sup>19</sup>

The  $H^E$  vs.  $X_1$  curve of water +1,4-dioxane is S-shaped with positive values at low mole fractions of water and negative values in the water rich region, of the order of  $\pm 520 \text{ J mol}^{-1}$  at 298.15 K.<sup>20</sup> The positive values are due to the breakdown of water associates and the negative are due to unlike H-bonding between water molecules and 1,4-dioxane. These effects contribute both to the negative  $V^E$  over the whole composition range. Therefore, in this system the interactional factor predominate (negative  $V^E$  and positive  $\Delta\eta$ ).

The  $V^E$  values increase with increasing temperature and  $\Delta\eta$  has an opposite trend.

As it was mentioned in literature,<sup>21</sup> positive  $G^{*E}$  values indicates the presence of strong interactions, whereas negative  $G^{*E}$  values suggest weak specific interactions between molecules in the mixture. The strong positive  $G^{*E}$  values for the water+1,4-dioxane system (maximum of about  $2200 \text{ J mol}^{-1}$  at 293.15 K), moderate positive values of  $G^{*E}$  for the water+EG system (maximum of about  $200 \text{ J mol}^{-1}$  at 293.15 K) and negative  $G^{*E}$  values for the 1,4-dioxane+EG system (minimum of about  $-800 \text{ J mol}^{-1}$  at 293.15 K) are in accordance with the above statement.

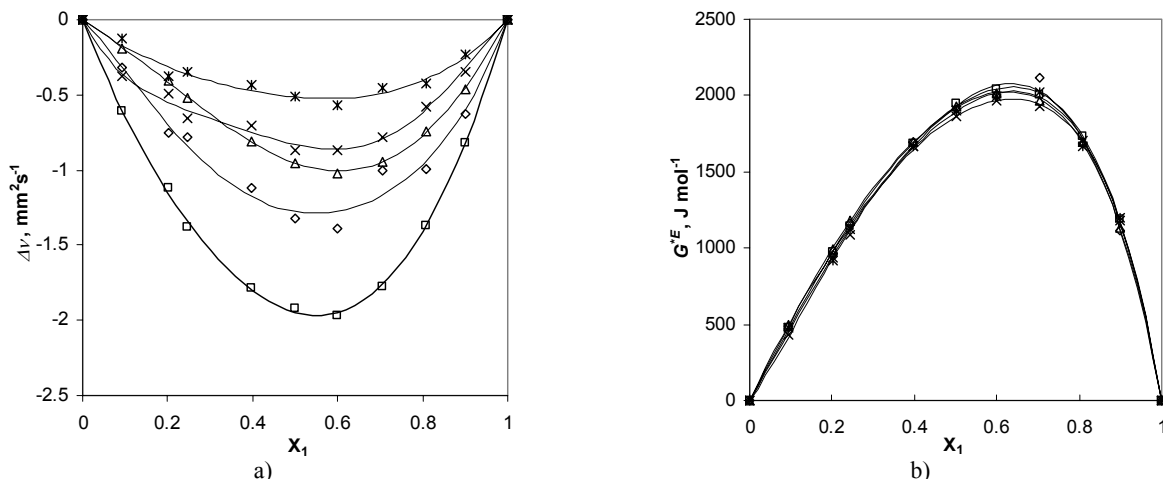


Fig. 1 – (a) Viscosity deviations and (b) excess Gibbs energy of activation of viscous flow  $G^{*E}$  for water (1)+EG (2) system at: (□) 293.15K, (◇) 298.15K, (Δ) 303.15K, (x) 308.15K, (\*) 313.15K; (–) Redlich-Kister's correlation

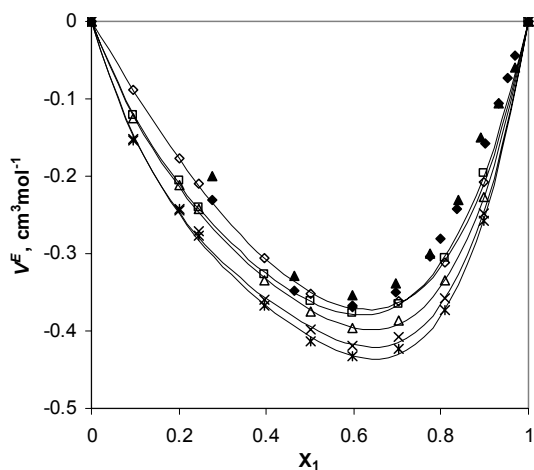


Fig. 2 – Excess molar volumes for water (1)+ EG (2) system at: (□) 293.15K, (◇) 298.15K, (Δ) 303.15K, (x) 308.15K, (\*) 313.15K; data at 293.15 K of (◆) Tzierkezos and Molinou<sup>7</sup> and (▲) Yang *et al.*<sup>8</sup>, (–) Redlich-Kister's correlation.

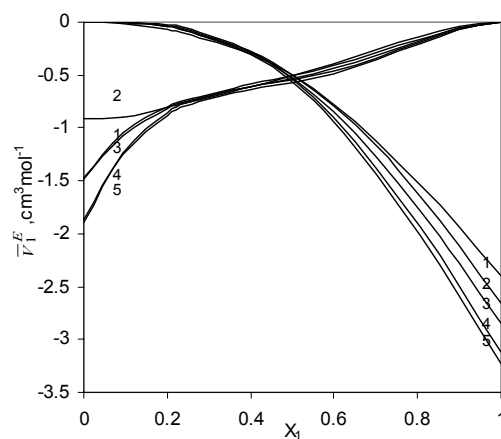


Fig. 3 – Partial molar volumes for water (1)+ EG (2) system at different temperatures; curves 1-5 represent the values at T=293.15, 298.15, 303.15, 308.15, 313.15 K; (–) Redlich Kister's correlation.

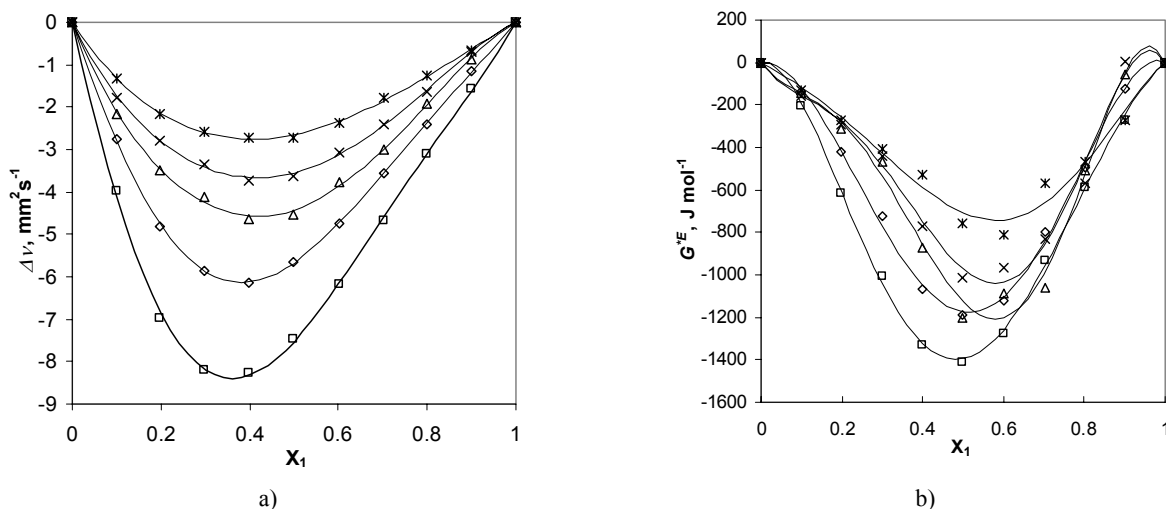


Fig. 4 – (a) Viscosity deviations and (b) excess Gibbs energy of activation of viscous flow  $G^{*E}$  for 1,4-dioxane (1)+EG (2) system at: (□) 293.15K, (◇) 298.15K, (Δ) 303.15K, (x) 308.15K, (\*) 313.15K; (–) Redlich-Kister's correlation.

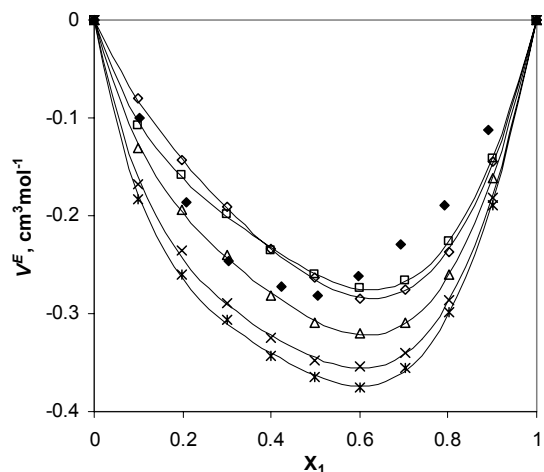


Fig. 5 – Excess molar volumes for 1,4-dioxane (1)+EG (2) system at ( $\square$ ) 293.15K, ( $\diamond$ ) 298.15K, ( $\Delta$ ) 303.15K, ( $\times$ ) 308.15K, ( $*$ ) 313.15K; data at 298.15 K of ( $\blacklozenge$ ) Nayak *et al.*<sup>5</sup>; (–) Redlich-Kister's correlation.

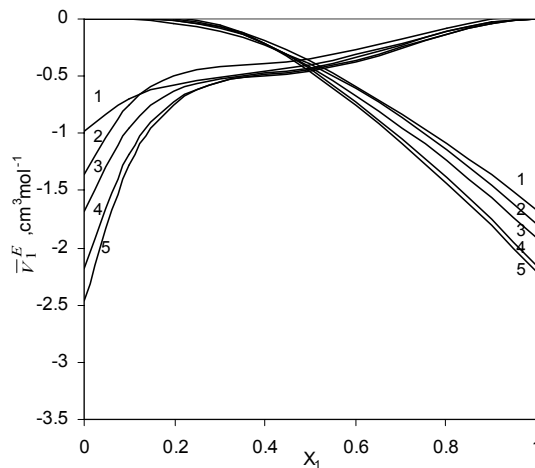


Fig. 6 – Partial molar volumes for 1,4-dioxane (1)+EG (2) system at different temperatures; curves 1-5 represent the values at T=293.15, 298.15, 303.15, 308.15, 313.15 K; (–) Redlich-Kister's correlation.

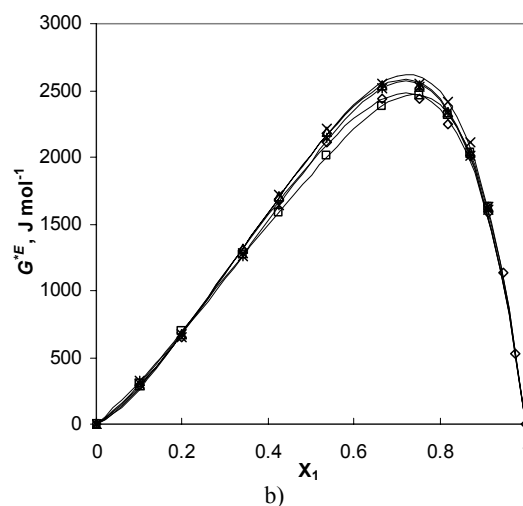
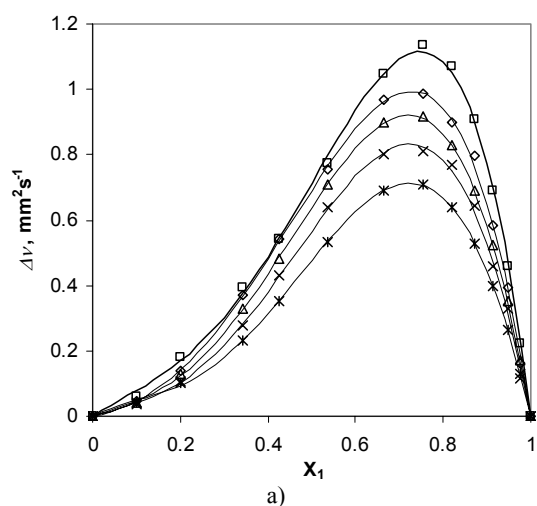


Fig. 7 – (a) Viscosity deviations and (b) excess Gibbs energy of activation of viscous flow  $G^{*E}$  for water (1)+1,4-dioxane (2), system at ( $\square$ ) 293.15K, ( $\diamond$ ) 298.15K, ( $\Delta$ ) 303.15K, ( $\times$ ) 308.15K, ( $*$ ) 313.15K; (–) Redlich-Kister's correlation.

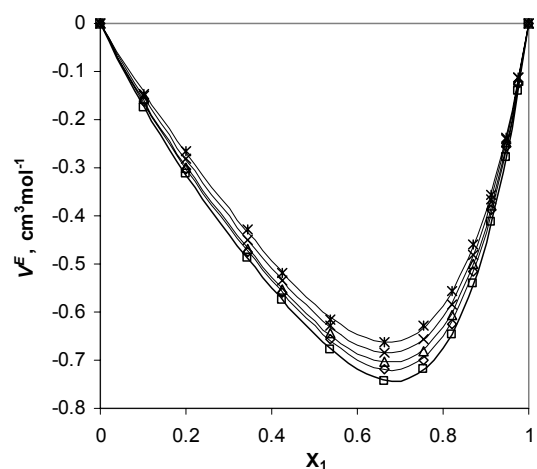


Fig. 8 – Excess molar volumes for water (1)+1,4-dioxane (2) system at ( $\square$ ) 293.15K, ( $\diamond$ ) 298.15K, ( $\Delta$ ) 303.15K, ( $\times$ ) 308.15K, ( $*$ ) 313.15K; (–) Redlich-Kister's correlation.

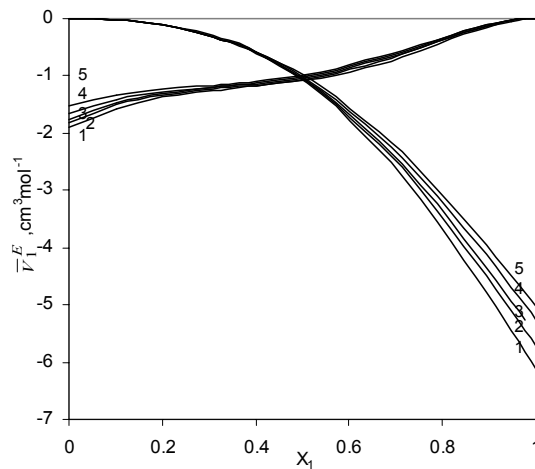


Fig. 9 – Partial molar volumes for water (1)+ 1,4-dioxane (2) system at different temperatures; curves 1-5 represent the values at T=293.15, 298.15, 303.15, 308.15, 313.15 K; (–) Redlich-Kister's correlation.

Table 3

The adjustable parameters and standard deviation of the excess functions for the binary systems at different temperatures

Function	$A_0$	$A_1$	$A_2$	$A_3$	$\sigma$	Function	$A_0$	$A_1$	$A_2$	$A_3$	$\sigma$
<b>water +EG</b>											
<b>T=293.15 K</b>						<b>T=308.15 K</b>					
$\Delta v/ \text{mm}^2 \cdot \text{s}^{-1}$	-7.790	-1.536	-0.568	0.510	0.025	$\Delta v/ \text{mm}^2 \cdot \text{s}^{-1}$	-3.326	-1.299	-0.870	2.626	0.039
$G^{*E}/ \text{kJ} \cdot \text{mol}^{-1}$	7.711	3.547	2.384	1.815	0.012	$G^{*E}/ \text{kJ} \cdot \text{mol}^{-1}$	7.451	3.159	2.369	2.926	0.016
$V^E/ \text{cm}^3 \cdot \text{mol}^{-1}$	-1.440	-0.556	-0.494	0.096	0.003	$V^E/ \text{cm}^3 \cdot \text{mol}^{-1}$	-1.571	-0.615	-0.932	0.003	0.006
<b>T=298.15 K</b>						<b>T=313.15 K</b>					
$\Delta v/ \text{mm}^2 \cdot \text{s}^{-1}$	-5.112	-0.921	-0.170	-1.323	0.087	$\Delta v/ \text{mm}^2 \cdot \text{s}^{-1}$	-2.063	-0.519	-0.507	0.090	0.041
$G^{*E}/ \text{kJ} \cdot \text{mol}^{-1}$	7.719	4.041	2.181	0.158	0.045	$G^{*E}/ \text{kJ} \cdot \text{mol}^{-1}$	7.581	3.586	2.338	1.826	0.034
$V^E/ \text{cm}^3 \cdot \text{mol}^{-1}$	-1.391	-0.638	-0.396	-0.230	0.001	$V^E/ \text{cm}^3 \cdot \text{mol}^{-1}$	-1.622	-0.673	-0.927	-0.011	0.006
<b>T=303.15 K</b>											
$\Delta v/ \text{mm}^2 \cdot \text{s}^{-1}$	-3.815	-1.969	0.325	0.336	0.009						
$G^{*E}/ \text{kJ} \cdot \text{mol}^{-1}$	7.673	3.244	2.300	1.572	0.006						
$V^E/ \text{cm}^3 \cdot \text{mol}^{-1}$	-1.483	-0.649	-0.680	-0.028	0.004						
<b>1,4-dioxane +EG</b>											
<b>T=293.15 K</b>						<b>T=308.15 K</b>					
$\Delta v/ \text{mm}^2 \cdot \text{s}^{-1}$	-30.077	22.483	-2.990	-8.044	0.086	$\Delta v/ \text{mm}^2 \cdot \text{s}^{-1}$	-14.193	5.367	1.092	2.933	0.061
$G^{*E}/ \text{kJ} \cdot \text{mol}^{-1}$	-5.656	0.533	6.365	-0.272	0.011	$G^{*E}/ \text{kJ} \cdot \text{mol}^{-1}$	-3.855	-2.096	3.650	-2.675	0.042
$V^E/ \text{cm}^3 \cdot \text{mol}^{-1}$	-1.038	-0.450	-0.494	0.310	0.002	$V^E/ \text{cm}^3 \cdot \text{mol}^{-1}$	-1.380	-0.369	-0.788	0.385	0.005
<b>T=298.15 K</b>						<b>T=313.15 K</b>					
$\Delta v/ \text{mm}^2 \cdot \text{s}^{-1}$	-22.691	14.391	0.866	-4.944	0.037	$\Delta v/ \text{mm}^2 \cdot \text{s}^{-1}$	-10.611	4.281	-0.325	0.797	0.041
$G^{*E}/ \text{kJ} \cdot \text{mol}^{-1}$	-4.767	-0.456	6.487	-0.323	0.023	$G^{*E}/ \text{kJ} \cdot \text{mol}^{-1}$	-2.969	-2.499	3.981	8.109	0.037
$V^E/ \text{cm}^3 \cdot \text{mol}^{-1}$	-1.063	-0.524	-0.328	0.120	0.002	$V^E/ \text{cm}^3 \cdot \text{mol}^{-1}$	-1.453	-0.376	-0.882	0.509	0.004
<b>T=303.15 K</b>											
$\Delta v/ \text{mm}^2 \cdot \text{s}^{-1}$	-17.683	6.966	1.957	2.962	0.082						
$G^{*E}/ \text{kJ} \cdot \text{mol}^{-1}$	-4.539	-3.625	5.956	5.140	0.064						
$V^E/ \text{cm}^3 \cdot \text{mol}^{-1}$	-1.229	-0.461	-0.569	0.350	0.003						
<b>water+1,4-dioxane</b>											
<b>T=293.15 K</b>						<b>T=308.15 K</b>					
$\Delta v/ \text{mm}^2 \cdot \text{s}^{-1}$	2.849	4.653	2.951	0.281	0.018	$\Delta v/ \text{mm}^2 \cdot \text{s}^{-1}$	2.266	3.710	1.394	-0.499	0.017
$G^{*E}/ \text{kJ} \cdot \text{mol}^{-1}$	7.444	7.046	6.298	5.113	0.022	$G^{*E}/ \text{kJ} \cdot \text{mol}^{-1}$	8.059	8.068	5.306	4.043	0.046
$V^E/ \text{cm}^3 \cdot \text{mol}^{-1}$	-2.581	-1.742	-1.424	-0.360	0.002	$V^E/ \text{cm}^3 \cdot \text{mol}^{-1}$	-2.408	-1.643	-1.048	-0.152	0.002
<b>T=298.15 K</b>						<b>T=313.15 K</b>					
$\Delta v/ \text{mm}^2 \cdot \text{s}^{-1}$	2.765	4.142	1.731	0.087	0.015	$\Delta v/ \text{mm}^2 \cdot \text{s}^{-1}$	1.906	3.295	1.314	-0.853	0.004
$G^{*E}/ \text{kJ} \cdot \text{mol}^{-1}$	7.826	7.097	4.879	4.816	0.034	$G^{*E}/ \text{kJ} \cdot \text{mol}^{-1}$	7.831	8.159	5.528	2.925	0.034
$V^E/ \text{cm}^3 \cdot \text{mol}^{-1}$	-2.515	-1.717	-1.255	-0.227	0.004	$V^E/ \text{cm}^3 \cdot \text{mol}^{-1}$	-2.335	-1.595	-0.935	-0.162	0.004
<b>T=303.15 K</b>											
$\Delta v/ \text{mm}^2 \cdot \text{s}^{-1}$	2.555	4.029	1.463	-0.482	0.004						
$G^{*E}/ \text{kJ} \cdot \text{mol}^{-1}$	8.044	7.703	5.055	4.299	0.039						
$V^E/ \text{cm}^3 \cdot \text{mol}^{-1}$	-2.478	-1.645	-1.162	-0.240	0.004						



## CONCLUSIONS

New experimental data of kinematic viscosities and densities for the binary systems water+ethylene glycol and 1,4-dioxane+ethylene glycol at 298.15, 303.15, 313.15 and 323.15 K have been reported. The corresponding excess functions, excess molar volumes, viscosity deviations and excess Gibbs energy of activation of viscous flow for the above binary systems and for the water+1,4-dioxane system have been calculated and fitted to the Redlich-Kister equation. The excess molar volumes and deviations in viscosity are all negative for the binary mixtures water + ethylene glycol and 1,4-dioxane+ethylene glycol, which suggest that both hydrogen bonding and molecular sizes and shapes of the molecules are important for these systems, interactional factor being more important for the first one. The water + 1,4-dioxane system presents negative  $V^E$  values and positive  $\Delta\eta$  values, which indicate the predominance of the interactional effect over geometrical.

Also, the partial excess molar volumes ( $\bar{V}_i^E$ ) were calculated from the smoothed data excess functions. For all investigated systems, the partial excess molar volumes have been found negative for both components, with more accentuated difference between the infinite dilution values in the aqueous systems.

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