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Volumetric and viscosimetric measurements for methanol + CH$_3$-O-(CH$_2$CH$_2$O)$_n$-CH$_3$ (n = 2, 3, 4) mixtures at (293.15-303.15) K

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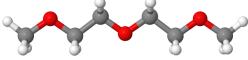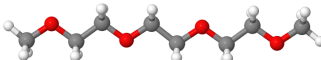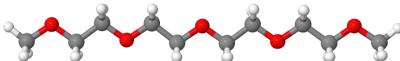
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ABSTRACT

Densities and kinematic viscosities of binary mixtures of methanol + 2,5,8-trioxanonane, or + 2,5,8,11-tetraoxadodecane, or + 2,5,8,11,14-pentaoxapentadecane have been measured over the whole composition range at 293.15, 298.15 and 303.15 K and atmospheric pressure. Densities were determined using a vibrating-tube density meter and viscosities were measured with an automatic Ubbelohde capillary viscometer. The experimental results have been used to calculate the excess molar volumes, V_m^E, and the deviations of dynamic viscosity, $\Delta\eta$. Moreover, viscosity data were correlated by some semi-empirical equations (Grunberg-Nissan, Hind, Frenkel, Katti-Chaudhri, McAllister and Heric). The large and negative V_m^E and the positive $\Delta\eta$ values obtained seem to remark the predominant contribution of free volume effects on interactional effects to these thermophysical properties.

1. Introduction

In the last years, the G.E.T.E.F. has carried out diverse experimental studies to determine the physical properties of different mixtures of great interest in chemical industry. Due to their strongly negative deviations from Raoult's law, the study of liquid mixtures involving two self-associated compounds, as 1-alkanol + alkylamine, has become one of the main investigation lines of the group. In this work, we have studied the volumetric and viscosimetric behavior of methanol + $CH_3-O-(CH_2CH_2O)_n-CH_3$ binary mixtures over the entire concentration range at different temperatures, also expecting deviations from the Raoult's law, but positive in this case.

Interest on alcohol + ether mixtures is consequence of their wide variety of applications. For example, this type of systems are increasingly added to gasolines to increase their octane number and decrease carbon monoxide emissions [1, 2]. These mixtures are also taken into account for the research on new working fluid pairs for use in absorption refrigeration systems and heat transformers. The selection of a suitable substance can be made by a systematic study of its physical and thermodynamic properties. The NH_3 + H_2O and H_2O + LiBr working pairs are well known in refrigeration technology, but show important disadvantages due to higher temperature levels of the heat transformer process. Moreover, for H_2O + LiBr there are problems of corrosion and crystallization which can be reduced only by the addition of inhibitors. Therefore, organic mixtures as the absorbent like polyethylene glycols (PEG) with other polar organic molecules like alcohols have been suggested [3]. Alkanol + ether mixtures are also industrially relevant because alkanols are basic components in the synthesis of oxaalkanes and therefore are contained as an impurity. On

Table 1
Source, purity and molecular structure of every compound.

Compound	Molecular structure	Source	Mass fraction purity
Methanol		Sigma-Aldrich	0.998
2,5,8-Trioxanonane		Fluka	0.990
2,5,8,11-Tetraoxadodecane		Fluka	0.980
2,5,8,11,14-Pentaoxapentadecane		Fluka	0.980

the other hand, mixtures of short chain 1-alkanols with linear polyethers can be considered as simple models of the complex systems water + PEG, widely used in biochemical and biomedical processes [4]. From a theoretical point of view, the study of 1-alkanol + ether mixtures is particularly important due to their complexity, related to the partial destruction of the H-bonds between alcohol molecules by the active ether molecules, and to the new OH–O bonds created upon mixing [5, 6]. In addition, in solutions formed by 1-alkanol and a linear polyether, strong dipole-dipole interactions can be expected.

In this work, the densities, ρ, and kinematic viscosities, ν, of homogeneous binary mixtures formed by methanol + $CH_3-O-(CH_2CH_2O)_n-CH_3$ have been measured at 293.15, 298.15 and 303.15 K and atmospheric pressure. The results were used to calculate excess molar volumes, V_m^E, and changes of dynamic viscosity on mixing, $\Delta\eta$, over the entire mole fraction range. Several methods to correlate the viscosity data of mixtures were applied to test their validity in our systems, namely Grunberg-Nissan [7], Hind [8], Frenkel [9], Katti-Chaudhri [10], McAllister [11] and Heric [12]. Some experimental results on the studied mixtures are already available in the literature: V_m^E for methanol + 2,5,8-trioxanonane at 298.15 K [13, 14], V_m^E for methanol + 2,5,8,11-tetraoxadodecane at 298.15 K [13], V_m^E for methanol + 2,5,8,11,14-pentaoxapentadecane at 293.15 K [15, 16], 298.15 K [13] and 303.15 K [15, 16], and η (dynamic viscosity) at 293.15 K and 303.15 K for the previous system [15].

2. Experimental

Information on source and purity of pure compounds used in this work is contained in Table 1. All liquids were kept over 3 Å molecular sieves to reduce the water content and protected against atmospheric moisture and CO_2. The purity of each component was evaluated by comparing the measured values of density and dynamic viscosity with those reported in the literature (Table 2).

Binary mixtures were prepared by mass in small vessels of about 10 cm^3. The composition of the mixtures studied is characterized by the value of the mole fraction of one of the components, methanol in our case. To estimate the

Table 2
Physical properties of pure compounds at 293.15, 298.25 and 303.15 K and atmospheric pressure*.

Property	T/K	Methanol		2,5,8-Trioxanonane		2,5,8,11-Tetraoxadodecane		2,5,8,11,14-Pentaoxapentadecane	
		Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
ρ/g·cm^{-3}	293.15	0.791576	0.79190[a]	0.944138	0.9434[d]	0.986165	0.98416[f]	1.011350	1.01106[h]
			0.79109[b]		0.9452[k]		0.9860[j]		1.0123[j]
			0.79154[c]		0.9438[k]		0.9846[j]		1.0115[j]
	298.15	0.786872	0.78720[a]	0.939171	0.9385[d]	0.981408	0.97961[f]	1.006723	1.00707[h]
			0.78648[b]		0.9402[j]		0.9815[j]		1.0076[j]
			0.78683[c]		0.9388[j]		0.9799[j]		1.0068[j]
	303.15	0.782140	0.78248[a]	0.934206	0.9335[d]	0.976657	0.97485[f]	1.002114	1.00249[h]
			0.78122[b]		0.9352[j]		0.9767[j]		1.0031[j]
			0.78212[c]		0.9338[j]		0.9751[j]		1.0022[j]
η/mPa·s	293.15	0.590	0.585[a]	1.080	1.09[e]	2.188	2.19[g]	3.817	3.83[i]
			0.593[b]		1.081[j]		2.162[j]		3.846[j]
			0.582[c]						
	298.15	0.551	0.545[a]	0.997	0.998[e]	1.974	1.96[g]	3.378	3.38[i]
			0.551[b]		1.011[j]		1.956[j]		3.335[j]
			0.550[c]						
	303.15	0.506	0.508[a]	0.916	0.914[e]	1.777	1.78[g]	2.985	3.00[i]
			0.509[b]		0.942[j]		1.777[j]		2.967[j]
			0.512[c]						

*Standard and relative standard uncertainties are: $u(T) = 0.02$ K, $u(p) = 1$ kPa, $u_r(\rho) = 0.0012$ and $u_r(\eta) = 0.01$.
[a][17], [b][18], [c][19], [d][20], [e][21], [f][22], [g][23], [h][24], [i][25], [j][26].

volume V_i of each liquid necessary to obtain a given mole fraction x'_1, ideal additive is assumed ($V_{aprox} = V_1 + V_2$). This leads easily to the following equation:

$$V_1 = \frac{M_1 \rho_2 x'_1 V_{aprox}}{M_1 \rho_2 x'_1 + M_2 \rho_1 \left(1 - x'_1\right)} \tag{1}$$

The procedure to prepare the mixture was the following. Firstly, the empty bottle was weighed and the less volatile component was introduced by means of a syringe. After weighing the bottle loaded with the first component, the more volatile one was added similarly and the bottle was weighed again. All weighing were performed using a balance Mettler Toledo AE 240 with ±0.02 mg accuracy. Once the mixture is done, the real molar fraction must be calculated. It will usually differ from the estimated one due to the non-additivity of volumes and the inaccuracy of the syringes.

The real mole fraction in terms of the mass can be determined as:

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \tag{2}$$

Caution was taken to prevent evaporation, and the error in the final mole fraction is estimated to be ± 0.0001. Conversion to molar quantities was based on the relative atomic mass Table of 2013 issued by IUPAC [27].

2.1. Density measurements

The densities of both pure liquids and mixtures were measured using a vibrating-tube densimeter Anton Paar DMA 602. The history of the vibrating-tube densimeter traces back to the work by Kratky *et al.* [28] in the late 1960's. The principle of density measurement is based on a constant relation between the density of fluid inside the vibrating tube, ρ, and the vibration period, τ. The measuring cell consists of an oscillator formed by an hallow U-shaped borosilicate glass tube, a chemically inert material, that comprises about 1.5 cm^3 of the sample. The U-tube is completely enclosed in an envelope, containing a high thermal conductivity gas. This envelope is surrounded by a glass jacket, through which a thermostated liquid is circulated. By this means, the temperature equilibration time is widely reduced. The remaining instrumentation consists of a system of electronic excitement and electrical components that provide a signal transmission of the period for the processor unit. The instrument applies an external electromagnetic force to balance the damping forces on the oscillating tube. While this force balance is maintained, the resonant oscillations of the system are established. The period of the resonance oscillations is then measured and related to the density of the liquid. The vibration amplitude of the tube is so small that the mode of vibration can be regarded as a simple harmonic oscillation. Thus, the motion of the oscillator may be described by the simple mass spring model. The resonant period of a mass performing an undamped oscillation is given by Eq. (3):

$$\tau = 2\pi\sqrt{m/k} \tag{3}$$

where k is the spring constant and m is the total mass, which in our case is:

$$m = M_0 + \rho V_0 \tag{4}$$

M_0 is the effective mass of the empty vibrator and V_0 is the volume of the sample taking part in the motion. Substituting Eq. (4) into Eq. (3), applying the square and isolating ρ, the expression can be rewritten as follows:

$$\rho = A + B\tau^2 \tag{5}$$

where A and B are determined in the instrument calibration. Since the calibration constant A is more susceptible to change over time, the density of a reference compound is taken from the literature and its characteristic period is

determined every session by means of the equation:

$$\rho_{\text{ref}} = A + B\tau_{\text{ref}}^2$$ (6)

Subtracting Eq. (5) from Eq. (6) we obtain:

$$\rho = \rho_{\text{ref}} + B\left(\tau^2 - \tau_{\text{ref}}^2\right)$$ (7)

By this expression the influence of temporary changes in the calibration constant is eliminated. The vibrating-tube densimeter Anton Paar DMA 602 was automatically thermostated within ± 0.01 K by means of a LAUDA RE 304 heating bath. The temperature was measured using a PT100 temperature probe inside the instrument. The oscillation period τ was measured with a Philips PM 6669 frequency meter. This was counted with eight digits, which were integrated and renewed every 10 s. Each value of τ was obtained from an average of 80 measures.

The calibration of the densimeter was carried out with deionised double-distilled water, isooctane, heptane, cyclohexane, 1-propanol and benzene, using the density values from the literature [29–32]. Details on the calibration procedure have been previously reported [33, 34]. Ethanol and acetone were used for rinsing the cell tube between measurements. The reproducibility of ρ measurements is $5 \cdot 10^{-3}$ kg·m^{-3} apart from the errors due to calibration and the density of the reference liquids. The excess molar volumes were calculated from the densities of the pure liquids and their mixtures. The accuracy in V_{m}^{E} is believed to be less than $\pm (0.01|V_{\text{m,min}}^{\text{E}}| + 0.005)$ cm^3·mol^{-1}, where $|V_{\text{m,min}}^{\text{E}}|$ denotes the minimum experimental value of the excess molar volume with respect to x_1.

2.2. Viscosity measurements

Kinematic viscosities, ν, were determined using two Ubbelohde viscosimeters (type I and Ic) with a Schoot-Geräte automatic measuring unit model AVS-350. An electronic stopwatch with an accuracy of ± 0.01 s was used for measuring efflux times. The temperature was kept constant within ± 0.01 K by means of a controller bath CT52, also from Schott. The calibration of the viscosimeters was carried out with heptane, octane, decane, 1-propanol, 1-butanol and 1-pentanol, using the density values from the literature [31, 32, 35–37]. Further details on calibration procedure can be found elsewhere [38].

Considering the corrections for kinetic energy and the end effect from the Hagen–Poiseuille law describing a laminar steady flow of a Newtonian fluid through a capillary under gravity, the following formula for the capillary viscometer can be stated [39]:

$$\nu = \frac{\pi r^4 g h}{8V(L + nr)}t - \frac{mV}{8\pi(L + nr)t}$$ (8)

where r is the capillary radius, V is the volume of the timing bulb, T is the efflux time and L is the length of the capillary. In this equation, n is a coefficient of the end correction and its value is approximately 1 [40], thus $L + nr$ can be approximated to L considering $L \geqslant r$ for viscometers with long capillaries. The second term in this equation is the kinetic energy correction and m is its coefficient, which depends on the shape of the capillary ends and also on

the flow condition of the Reynolds number, Re. In the range of low Re and for trumpet-shaped capillary ends such as for the viscometer used in this work, m approaches zero with decreasing Re, and the equation can be rewritten in the following form obtained through the experimental investigation of Cannon *et al.* [41]:

$$v = Kt - \frac{E}{t^2} \tag{9}$$

This equation was accepted by the ISO in 1994 [42]. The kinematic viscosity is a quantity in which no force is involved. Dynamic viscosity can be obtained by multiplying the absolute viscosity of a fluid with the fluid mass density like:

$$\eta = v \cdot \rho \tag{10}$$

The dynamic viscosity is a measure of internal resistance. It represents the tangential force per unit area required to move one horizontal plane with respect to another plane at an unit velocity when maintaining an unit distance apart in the fluid. For those particularly interested in the interaction between molecules that can be interpreted in terms of mechanical stress, which is our case, the most appropriate magnitude is the dynamic viscosity. Nevertheless, the kinematic viscosity is recommended when interested in fluid motion and velocity field. We have estimated the relative standard uncertainty of the v and η measurements to be 1%. For the deviations of dynamic viscosity from linear dependence on molar fraction, $\Delta\eta$, such uncertainty is 2%.

3. Experimental results and correlations

The results of densities and dynamic viscosities as a function of mole fraction of the alcohol, x_1, are collected in Table 3.

The excess molar volumes and changes of viscosity on mixing have also been calculated. The excess volume can be calculated using the following equation:

$$V_{\mathrm{m}}^{\mathrm{E}} = \frac{M_1 x_1 + M_2 x_2}{\rho} - \frac{M_1 x_1}{\rho_1} - \frac{M_2 x_2}{\rho_1} \tag{11}$$

where ρ is the density of the mixture and M_i, x_i, ρ_i are the molecular weight, mole fraction and density of pure components. The viscosity deviation is calculated by the following equation:

$$\Delta\eta = \eta - \left(x_1 \eta_1 - x_2 \eta_2 \right) \tag{12}$$

in which η represents the dynamic viscosity of the mixture, x_i the mole fraction of each component and η_i their dynamic viscosity.

The results of $V_{\mathrm{m}}^{\mathrm{E}}$ and $\Delta\eta$ were fitted by unweighted least-squares polynomial regression to the Redlich-Kister

Table 3

Densities, ρ, excess molar volumes, V_m^E, dynamic viscosities, η, and deviations of viscosity from linear dependence on mole fraction, $\Delta\eta$, for methanol (x_1) + linear polyether $(1 - x_1)$ systems at various temperatures and atmospheric pressure*.

x_1	$\rho/\mathrm{g \cdot cm^{-3}}$	$V_m^E/\mathrm{cm^3 \cdot mol^{-1}}$	$\eta/\mathrm{mPa \cdot s}$	$\Delta\eta/\mathrm{mPa \cdot s}$
Methanol (x_1) + 2,5,8-trioxanonane $(1 - x_1)$; T = 293.15 K				
0.0560	0.942328	−0.1049	1.065	0.012
0.1076	0.940435	−0.1900	1.050	0.023
0.2020	0.936398	−0.3273	1.015	0.041
0.2929	0.931629	−0.4334	0.990	0.054
0.3965	0.924931	−0.5333	0.951	0.066
0.4979	0.916514	−0.5964	0.909	0.073
0.5993	0.905508	−0.6235	0.863	0.077
0.6891	0.892496	−0.5976	0.814	0.072
0.7967	0.870965	−0.5127	0.748	0.058
0.8412	0.859143	−0.4447	0.718	0.050
0.8996	0.839967	−0.3285	0.674	0.035
0.9480	0.819736	−0.1979	0.637	0.022
Methanol (x_1) + 2,5,8-trioxanonane $(1 - x_1)$; T = 298.15 K				
0.0560	0.937345	−0.1032	0.984	0.012
0.1076	0.935453	−0.1891	0.970	0.022
0.2020	0.931422	−0.3281	0.940	0.039
0.2929	0.926647	−0.4339	0.916	0.050
0.3965	0.919956	−0.5350	0.882	0.062
0.4979	0.911565	−0.6006	0.843	0.068
0.5993	0.900571	−0.6278	0.800	0.071
0.6891	0.887569	−0.6012	0.756	0.066
0.7967	0.866088	−0.5168	0.697	0.056
0.8412	0.854281	−0.4479	0.669	0.047
0.8996	0.835188	−0.3335	0.629	0.033
0.9480	0.814960	−0.1993	0.595	0.020
Methanol (x_1) + 2,5,8-trioxanonane $(1 - x_1)$; T = 303.15 K				
0.0560	0.932376	−0.1035	0.904	0.011
0.1076	0.930473	−0.1884	0.891	0.019
0.2020	0.926432	−0.3272	0.863	0.035
0.2929	0.921657	−0.4339	0.840	0.044
0.3965	0.914955	−0.5343	0.809	0.055
0.4979	0.906593	−0.6032	0.775	0.063
0.5993	0.895612	−0.6311	0.735	0.065
0.6891	0.882643	−0.6059	0.693	0.060

Table 3
(Continuation.)

x_1	$\rho/\text{g·cm}^{-3}$	$V_\text{m}^\text{E}/\text{cm}^3\text{·mol}^{-1}$	$\eta/\text{mPa·s}$	$\Delta\eta/\text{mPa·s}$
0.7967	0.861187	−0.5205	0.641	0.052
0.8412	0.849420	−0.4524	0.615	0.045
0.8996	0.830353	−0.3364	0.578	0.031
0.9480	0.810177	−0.2018	0.546	0.019
Methanol (x_1) + 2,5,8,11-tetraoxadodecane ($1 - x_1$); T = 293.15 K				
0.0543	0.984278	−0.1025	2.129	0.028
0.0988	0.982559	−0.1801	2.084	0.054
0.1978	0.978232	−0.3523	1.982	0.110
0.3013	0.972620	−0.5117	1.864	0.158
0.3994	0.965819	−0.6303	1.737	0.188
0.5183	0.954710	−0.7167	1.570	0.211
0.5962	0.945145	−0.7546	1.443	0.208
0.6983	0.927936	−0.7317	1.260	0.188
0.7969	0.903693	−0.6527	1.055	0.141
0.8472	0.886395	−0.5595	0.944	0.110
0.8993	0.863294	−0.4330	0.825	0.074
0.9489	0.833866	−0.2622	0.711	0.040
Methanol (x_1) + 2,5,8,11-tetraoxadodecane ($1 - x_1$); T = 298.15 K				
0.0543	0.979509	−0.1017	1.922	0.025
0.0988	0.977785	−0.1795	1.882	0.049
0.1978	0.973463	−0.3550	1.795	0.102
0.3013	0.967843	−0.5157	1.690	0.144
0.3994	0.961057	−0.6381	1.580	0.174
0.5183	0.949935	−0.7245	1.433	0.197
0.5962	0.940344	−0.7606	1.321	0.195
0.6983	0.923153	−0.7397	1.158	0.178
0.7969	0.898910	−0.6600	0.975	0.135
0.8472	0.881607	−0.5651	0.875	0.107
0.8993	0.858526	−0.4380	0.767	0.073
0.9489	0.829121	−0.2654	0.662	0.038
Methanol (x_1) + 2,5,8,11-tetraoxadodecane ($1 - x_1$); T = 303.15 K				
0.0543	0.974750	−0.1019	1.733	0.025
0.0988	0.973032	−0.1817	1.696	0.044
0.1978	0.968727	−0.3625	1.621	0.095
0.3013	0.963071	−0.5202	1.527	0.132
0.3994	0.956308	−0.6479	1.434	0.164

Table 3
(Continuation.)

x_1	$\rho/\text{g·cm}^{-3}$	$V_m^E/\text{cm}^3\text{·mol}^{-1}$	$\eta/\text{mPa·s}$	$\Delta\eta/\text{mPa·s}$
0.5183	0.945165	−0.7335	1.302	0.184
0.5962	0.935540	−0.7669	1.203	0.184
0.6983	0.918364	−0.7482	1.058	0.169
0.7969	0.894125	−0.6682	0.894	0.130
0.8472	0.876812	−0.5715	0.804	0.104
0.8993	0.853748	−0.4437	0.705	0.071
0.9489	0.824370	−0.2697	0.608	0.038
Methanol (x_1) + 2,5,8,11,14-pentaoxapentadecane ($1 - x_1$); T = 293.15 K				
0.0463	1.009937	−0.1123	3.726	0.058
0.1031	1.008010	−0.2428	3.616	0.131
0.1978	1.004110	−0.4232	3.408	0.229
0.3111	0.997983	−0.5766	3.132	0.319
0.3886	0.992774	−0.6740	2.919	0.356
0.4940	0.983710	−0.7807	2.592	0.369
0.5935	0.972005	−0.8430	2.250	0.348
0.6966	0.954669	−0.8581	1.868	0.299
0.7966	0.928658	−0.7800	1.467	0.221
0.8472	0.909651	−0.6981	1.244	0.161
0.8972	0.884032	−0.5460	1.024	0.103
0.9495	0.846553	−0.3371	0.803	0.050
Methanol (x_1) + 2,5,8,11,14-pentaoxapentadecane ($1 - x_1$); T = 298.15 K				
0.0463	1.005320	−0.1162	3.301	0.053
0.1031	1.003388	−0.2476	3.209	0.122
0.1978	0.999465	−0.4267	3.036	0.217
0.3111	0.993318	−0.5802	2.803	0.304
0.3886	0.988100	−0.6788	2.611	0.332
0.4940	0.979020	−0.7865	2.326	0.344
0.5935	0.967301	−0.8500	2.031	0.330
0.6966	0.949975	−0.8685	1.697	0.288
0.7966	0.923955	−0.7905	1.344	0.218
0.8472	0.904927	−0.7068	1.145	0.162
0.8972	0.879332	−0.5551	0.948	0.106
0.9495	0.841832	−0.3419	0.744	0.050
Methanol (x_1) + 2,5,8,11,14-pentaoxapentadecane ($1 - x_1$); T = 303.15 K				
0.0463	1000703	−0.1164	2.916	0.046
0.1031	0.998764	−0.2485	2.845	0.116

Table 3
(Continuation.)

x_1	ρ/g·cm^{-3}	V_m^E/cm^3·mol^{-1}	η/mPa·s	$\Delta\eta$/mPa·s
0.1978	0.994828	−0.4289	2.691	0.197
0.3111	0.988666	−0.5839	2.493	0.280
0.3886	0.983427	−0.6819	2.333	0.312
0.4940	0.974340	−0.7925	2.089	0.329
0.5935	0.962606	−0.8575	1.829	0.316
0.6966	0.945281	−0.8790	1.537	0.280
0.7966	0.919251	−0.8016	1.225	0.215
0.8472	0.900209	−0.7167	1.047	0.163
0.8972	0.874625	−0.5647	0.871	0.111
0.9495	0.837107	−0.3479	0.683	0.052

*Standard uncertainties are: $u(T) = 0.02$ K, $u(p) = 1$ kPa and $u(x_1) = 0.0008$. Relative combined expanded standard uncertainties (0.95 level of confidence) are: $U_\mathrm{rc}(\rho) = 0.0024$, $U_\mathrm{rc}(\eta) = 0.02$, $U_\mathrm{rc}(V_\mathrm{m}^\mathrm{E}) = 0.025$ and $U_\mathrm{rc}(\Delta\eta) = 0.04$.

polynomial equation:

$$M = x_1 x_2 \sum_{i=0}^{k} A_i \left(2x_1 - 1\right)^i \tag{13}$$

where $M = V_m^E$ or $\Delta\eta$ and A_i are the polynomial coefficients obtained through fitting the equation to the empirical data. A graphical representation of the experimental results at 298.15 K together with the smoothing curves are shown in Figure 1.1 and Figure 1.2. The number of coefficients k used for each mixture was determined by applying an F-test [43] at the 99.5% confidence level. When the results of the F-test were not convincing, the optimum number of coefficients was ascertained from an examination of the variation in standard deviation, given by:

$$\sigma (M) = \sqrt{\frac{1}{N - k} \sum \left(M_\mathrm{cal} - M_\mathrm{exp}\right)^2} \tag{14}$$

where N stands for the number of direct experimental values. Table 4 lists the parameters A_i obtained in the regression together with the standard deviations $\sigma (M)$.

3.1. Comparison with data available in the literature

V_m^E for methanol + 2,5,8-trioxanonane, + 2,5,8,11-tetraoxadodecane, and + 2,5,8,11,14-pentaoxapentadecane have been previously measured at 298.15 K by the G.E.T.E.F. [13], showing a good agreement with the present results. Villamañán *et al.* also measured V_m^E for methanol + 2,5,8-trioxanonane at 298.15 K [14], reporting V_m^E/cm^3·mol^{-1} = −0.624 at equimolar composition, which is lower than the value determined here (−0.5978 cm^3·mol^{-1}) but still acceptable. Our data for the system involving 2,5,8,11,14-pentaoxapentadecane at 293.15 K and 303.15 K are also in good agreement with the data available in the literature. At equimolar composition, we have V_m^E/cm^3·mol^{-1} =

Table 4
Values of the fitting coefficients A_i of Redlich–Kister polynomial equation (Eq. (13)) and standard deviations (Eq. (14)) for representation of some properties at various temperatures and atmospheric pressure for methanol + linear polyether systems.

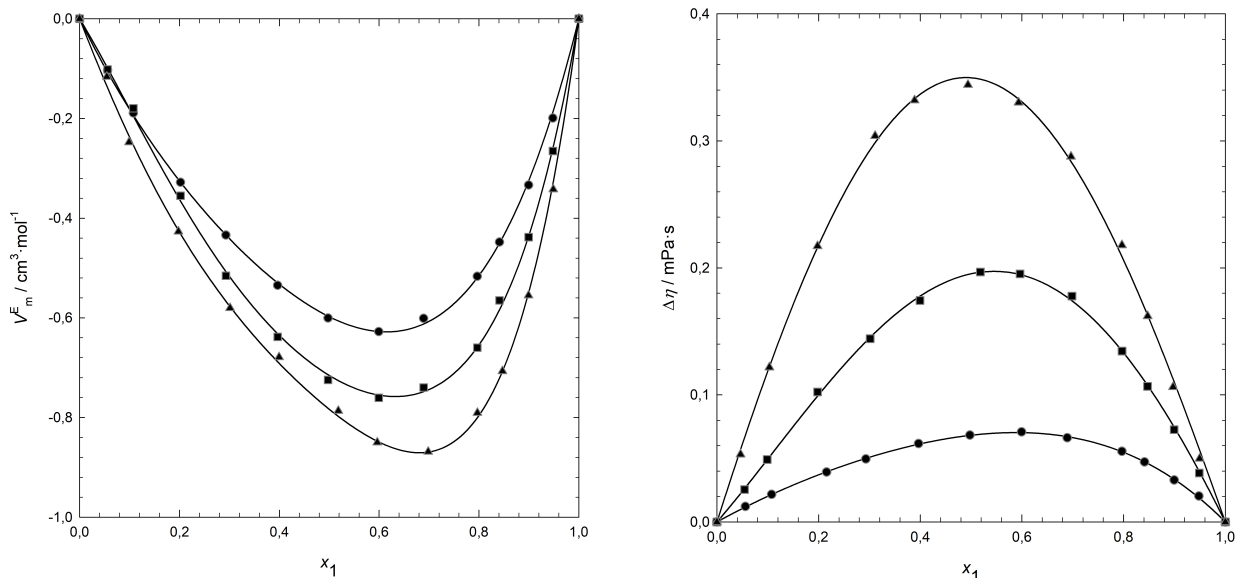| Property	A_0	A_1	A_2	A_3	$\sigma(M)$
Methanol (x_1) + 2,5,8-trioxanonane ($1 - x_1$); $T = 293.15$ K					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	−2.3779	−0.9656	−0.6524		0.006
$\Delta\eta/\text{mPa·s}$	0.294	0.099	0.029		0.001
Methanol (x_1) + 2,5,8-trioxanonane ($1 - x_1$); $T = 298.15$ K					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	−2.3912	−0.9891	−0.6513		0.006
$\Delta\eta/\text{mPa·s}$	0.273	0.092	0.039		0.001
$\Delta(\Delta G^*)/\text{J·mol}^{-1}$	3037	1351	590		6
Methanol (x_1) + 2,5,8-trioxanonane ($1 - x_1$); $T = 303.15$ K					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	−2.3986	−1.0164	−0.6630		0.006
$\Delta\eta/\text{mPa·s}$	0.249	0.094	0.040		0.001
Methanol (x_1) + 2,5,8,11-tetraoxadodecane ($1 - x_1$); $T = 293.15$ K					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	−2.8319	−1.2084	−0.8808	−0.8077	0.005
$\Delta\eta/\text{mPa·s}$	0.839	0.158	−0.180		0.002
Methanol (x_1) + 2,5,8,11-tetraoxadodecane ($1 - x_1$); $T = 298.15$ K					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	−2.8620	−1.2130	−0.8743	−0.8594	0.005
$\Delta\eta/\text{mPa·s}$	0.781	0.172	−0.146		0.002
$\Delta(\Delta G^*)/\text{J·mol}^{-1}$	5862	3235	1552		13
Methanol (x_1) + 2,5,8,11-tetraoxadodecane ($1 - x_1$); $T = 303.15$ K					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	−2.8947	−1.2076	−0.8961	−0.9058	0.005
$\Delta\eta/\text{mPa·s}$	0.733	0.186	−0.117		0.002
Methanol (x_1) + 2,5,8,11,14-pentaoxapentadecane ($1 - x_1$); $T = 293.15$ K					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	−3.1115	−1.5680	−1.8493	−0.8802	0.008
$\Delta\eta/\text{mPa·s}$	1.487	−0.117	−0.306		0.004
Methanol (x_1) + 2,5,8,11,14-pentaoxapentadecane ($1 - x_1$); $T = 298.15$ K					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	−3.1336	−1.6083	−1.9202	−0.8543	0.008
$\Delta\eta/\text{mPa·s}$	1.399	−0.063	−0.203		0.005
$\Delta(\Delta G^*)/\text{J·mol}^{-1}$	8346	4341	3138	2023	7
Methanol (x_1) + 2,5,8,11,14-pentaoxapentadecane ($1 - x_1$); $T = 303.15$ K					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	−3.1564	−1.6454	−1.9713	−0.8831	0.008
$\Delta\eta/\text{mPa·s}$	1.326	0.024	−0.162		0.004

Figure 1: (1) Excess molar volumes, V_m^E, and (2) deviations of viscosity, $\Delta\eta$, for methanol (x_1) + linear polyether $(1-x_1)$ mixtures at 298.15 K. Solid lines, results from the smoothing Eq. (13) with the coefficients listed in Table 4. Points, experimental data: ● 2,5,8-trioxanonane; ■ 2,5,8,11-tetraoxadodecane; ▲ 2,5,8,11,14-pentaoxapentadecane. All measurements were done at atmospheric pressure.

−0.7779 (293.15 K) and −0.7891 (303.15 K). Literature values, in the same units, are: −0.7810 [15] and −0.7895 [16] at 293.15 K, and −0.7916 [15] and −0.7790 [16] at 303.15 K. It is important to underline that the magnitude $A_p = \left(\partial V^E / \partial T\right)_p$ determined from V_m^E data for the system with the pentaether from reference [16] is positive at 298.15 K: $A_p(x_1 = 0.5)/\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 1.05 \cdot 10^{-3}$. Our measurements indicate that A_p is negative, $A_p(x_1 = 0.5)/\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = -1.1 \cdot 10^{-3}$, which is confirmed by the results from reference [15] ($-1.1 \cdot 10^{-3}$ $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ at the same conditions). The accurate determination of A_p values is crucial since the sign of this magnitude is closely related to interactional and structural effects, as we will see later. Finally, $\Delta\eta$ values found in the literature for the methanol + 2,5,8,11,14-pentaoxapentadecane system at 303.15 K are in good agreement with ours. At equimolar composition, $\Delta\eta/\text{mPa}\cdot\text{s} = 0.336$ [15], very similar to our value (0.329 mPa·s). However, $\Delta\eta$ values for the methanol + 2,5,8,11,14-pentaoxapentadecane system at 293.15 K reported in reference [15] largely differs from the results provided here. Thus, $\Delta\eta(x_1 = 0.5) = 0.181$ mPa·s [15] is much lower than our result (0.372 mPa·s). This may be due to, at the mentioned temperature, the viscosity of pure methanol given in reference [15], 0.985 mPa·s, is very different to those encountered in the literature (Table 2). Figure 2.1 and Figure 2.2 show a graphical comparison between our results and the literature data.
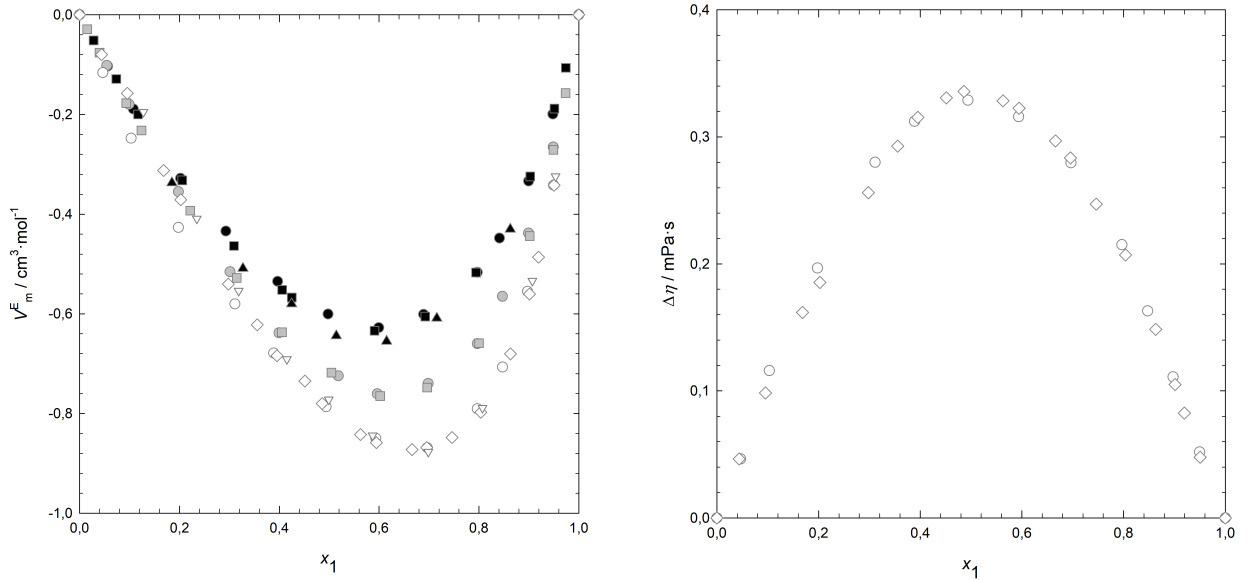
Figure 2: (1) Experimental data for excess molar volumes, $V_{\mathrm{m}}^{\mathrm{E}}$, for methanol $(x_1) + $ 2,5,8-trioxanonane $(1-x_1)$ mixtures at 298.15 K (● this work; ■ Carmona *et al.*; ▲ Villamañán *et al.*), $+$ 2,5,8,11-tetraoxadodecane mixtures at 298.15 K K (◐ this work; ▢ Carmona *et al.*), and $+$ 2,5,8,11,14-pentaoxapentadecane at 303.15 K (○ this work; ▽ Pereira *et al.*; ◇ Esteve *et al.*). (2) Experimental data for deviations of viscosity, $\Delta\eta$, for methanol $(x_1) + $ 2,5,8,11,14-pentaoxapentadecane $(1-x_1)$ at 303.15 K (○ this work; ◇ Esteve *et al.*). All measurements were done at atmospheric pressure.

4. Viscosity correlations

Viscosity data have been also correlated by means of some semi-empirical equations. For dynamic viscosities, the equations used are Grunberg-Nissan [7], Hind [8], Frenkel [9] and Katti-Chaudhri [10]. These semi-empirical equations have only one adjustable parameter. For kinematic viscosities, equations with two adjustable parameters have been applied, namely McAllister [11] and Heric [12] equations. The Grunberg–Nissan phenomenological equation is expressed as:

$$\eta = \exp\left(x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12}\right) \tag{15}$$

where G_{12} is a parameter proportional to the interchange energy and has been regarded as an indicator for the nonideal behavior of binary mixtures.

The semi-empirical equation due to Frenkel is:

$$\eta = x_1 \phi_1 \eta_1 + x_2 \phi_2 \eta_2 + 2\left(x_1 x_2 \phi_1 \phi_2\right)^{1/2} F_{12} \tag{16}$$

where F_{12} is an adjustable parameter.

Hind have proposed the following equation:

$$\ln \eta = x_1{}^2 \ln \eta_1 + x_2{}^2 \ln \eta_2 + 2 x_1 x_2 \ln \eta_{12} \tag{17}$$

where η_{12} is attributed to unlike pair interactions. This equation has been theoretically derived by Bearman and Jones [44] from statistical mechanical theory.

Katti and Chaudhri derived the following equation:

$$\ln \left(\eta V_{\mathrm{m}} \right) = x_1 \ln \left(\eta_1 V_{\mathrm{m},1} \right) + x_2 \ln \left(\eta_2 V_{\mathrm{m},2} \right) + x_1 x_2 \frac{W}{RT} \tag{18}$$

where W is an interaction term. All four above equations contain one adjustable parameter.

The two-parameter McAllister based on Eyring's theory of absolute reaction rates [45] and the three-body interaction model is given by:

$$
\begin{aligned}
\ln \nu = {}& x_1{}^3 \ln \nu_1 + 3 x_1{}^2 x_2 \ln \nu_{12} + 3 x_1 x_2{}^2 \ln \nu_{21} + x_2{}^3 \ln \nu_2 - \ln \left(x_1 + x_2 \frac{M_2}{M_1} \right) \\
& + 3 x_1{}^2 x_2 \ln \left(\frac{2}{3} + \frac{M_2}{3 M_1} \right) + 3 x_1 x_2{}^2 \ln \left(\frac{1}{3} + \frac{2 M_2}{3 M_1} \right) + x_2{}^3 \ln \left(\frac{M_2}{M_1} \right)
\end{aligned}
\tag{19}
$$

where ν_{12} and ν_{21} are interaction parameters and M_i and ν_i are the molecular mass and kinematic viscosity of pure component i.

The two parameter Heric and Brewer equation is of the form:

$$\ln \nu = x_1 \ln \left(\nu_1 M_1 \right) + x_2 \ln \left(\nu_2 M_2 \right) - \ln \left(x_1 M_1 + x_2 M_2 \right) + x_1 x_2 \left[\alpha_{12} + \left(x_1 - x_2 \right) \alpha_{21} \right] \tag{20}$$

where α_{12} and α_{21} are adjustable parameters. The correlating ability of each equation was tested by calculating the standard percentage deviations between the experimental and the calculated viscosity as:

$$\sigma_{\mathrm{r}} \left(F \right) = \sqrt{ \frac{1}{N - k} \sum \left(\frac{F_{\mathrm{cal}} - F_{\mathrm{exp}}}{F_{\mathrm{exp}}} \right)^2 } \tag{21}$$

where $F = \eta$ or ν. Values of the fitted parameters together with the standard deviations are collected in Table 5.

From the obtained results, we can conclude: (i) deviations between experimental results and model calculations increase with the ether size, i.e., when structural effects become more important (see below); (ii) Better results are obtained from the Hind equation; (iii) Results are not improved using equations with two adjustable parameters.

5. Discussion

Hereafter, we are referring to thermophysical properties of liquid mixtures at equimolar composition and 298.15 K.

Table 5
Fitted parameters from the semi-empirical equations used for the correlation of viscosities for methanol + linear polyether systems at various temperatures. Values in parentheses denote relative standard deviations by Eq. (21).

Grunberg-Nissan G_{12}	Hind η_{12}/mPa·s	Frenkel F_{12}/mPa·s	Katti-Chaudhri W/J·mol^{-1}	McAllister Z_{12}, Z_{21}/cSt	Heric-Brewer α_{12}, α_{21}
		Methanol (x_1) + 2,5,8-trioxanonane ($1 - x_1$); T = 293.15 K			
0.518	0.985	1.034	3144	1.231	0.818
(0.015)	(0.007)	(0.015)	(0.037)	1.049	0.093
				(0.008)	(0.008)
		Methanol (x_1) + 2,5,8-trioxanonane ($1 - x_1$); T = 298.15 K			
0.515	0.915	0.959	3186	1.149	0.810
(0.014)	(0.007)	(0.014)	(0.037)	0.977	0.087
				(0.008)	(0.008)
		Methanol (x_1) + 2,5,8-trioxanonane ($1 - x_1$); T = 303.15 K			
0.514	0.840	0.880	3239	1.066	0.824
(0.013)	(0.007)	(0.013)	(0.038)	0.898	0.117
				(0.009)	(0.009)
		Methanol (x_1) + 2,5,8,11-tetraoxadodecane ($1 - x_1$); T = 293.15 K			
1.302	1.796	2.178	6115	2.637	2.758
(0.072)	(0.012)	(0.072)	(0.090)	1.763	1.598
				(0.020)	(0.020)
		Methanol (x_1) + 2,5,8,11-tetraoxadodecane ($1 - x_1$); T = 298.15 K			
1.280	1.644	1.978	6151	2.426	2.729
(0.066)	(0.012)	(0.066)	(0.089)	1.6041	1.595
				(0.020)	(0.020)
		Methanol (x_1) + 2,5,8,11-tetraoxadodecane ($1 - x_1$); T = 303.15 K			
1.282	1.502	1.800	6258	2.242	2.754
(0.061)	(0.013)	(0.061)	(0.091)	1.449	1.644
				(0.021)	(0.021)
		Methanol (x_1) + 2,5,8,11,14-pentaoxapentadecane ($1 - x_1$); T = 293.15 K			
2.006	2.920	4.090	8957	5.603	4.768
(0.176)	(0.014)	(0.176)	(0.150)	2.623	3.308
				(0.042)	(0.042)
		Methanol (x_1) + 2,5,8,11,14-pentaoxapentadecane ($1 - x_1$); T = 298.15 K			
1.972	2.647	3.657	8990	5.046	4.695
(0.156)	(0.009)	(0.156)	(0.149)	2.358	3.258
				(0.043)	(0.043)
		Methanol (x_1) + 2,5,8,11,14-pentaoxapentadecane ($1 - x_1$); T = 303.15 K			
1.962	2.395	3.277	9114	4.622	4.712

Table 5
(Continuation.)

Grunberg-Nissan G_{12}	Hind η_{12}/mPa·s	Frenkel F_{12}/mPa·s	Katti-Chaudhri W/J·mol^{-1}	McAllister Z_{12},Z_{21}/cSt	Heric-Brewer α_{12},α_{21}
(0.144)	(0.006)	(0.144)	(0.151)	2.093	3.313
				(0.044)	(0.044)

5.1. Calorimetric data

The H_m^E/J·mol^{-1} values of methanol + polyether mixtures are positive and rather low. They change in the sequence: 338 ($n = 1$) [46] < 440 ($n = 2$) [47] < 581 ($n = 4$) [48]. Therefore, the contribution to H_m^E from the breaking of interaction between like molecules is dominant over the negative contribution related to the creation of alkanol-ether interactions upon mixing. On the other hand, both magnitudes H_m^E and n increase in line, which may be explained taking into account that the contribution to H_m^E from the disruption of ether-ether interactions also increases in line with n. In fact, for heptane mixtures we have H_m^E/J·mol^{-1} = 1285 ($n = 1$) [49] < 1621 ($n = 2$) [50] < 1754 ($n = 3$) [51] < 1891 ($n = 4$) [50]. It is to be noted that these values are much higher than those given above for the corresponding methanol systems, which underlines the importance of the interactions between unlike molecules. In the same sense, we must underline that the methanol + heptane system shows a miscibility gap at 298.15 K with an upper critical solution temperature at 324.1 K [52].

5.2. Volumetric data

The V_m^E/cm^3·mol^{-1} values of the methanol mixtures are rather large and negative. The variation with n is as follows: −0.4991 ($n = 1$) [13] > −0.5978 ($n = 2$) > −0.7155 ($n = 3$) > −0.7834 ($n = 4$) (this work). Interestingly, the signs of both excess functions H_m^E and V_m^E are opposite. This is typical of mixtures characterized by structural effects [53]. It is remarkable that, while H_m^E increases in line with n, V_m^E decreases. That is, structural effects become more important with the number of CH$_2$CH$_2$O groups involved in the ether. The mentioned structural effects may be of free volume type, since the difference between α_p values of the two mixture components also increases in line with n [54]. Thus, [α_p(methanol)−α_p(ether)]/10^{-3}·K^{-1}: −0.072 ($n = 1$) < 0.136 ($n = 2$) < 0.231 ($n = 3$) < 0.275 ($n = 5$) [31, 55]. In addition, the V_m^E curves become skewed towards higher mole fractions of methanol when the oxaalkane size increases (Figure 1.1), a normal behaviour of systems where structural effects exist.

The magnitude $A_p = \left(\partial V^E/\partial T\right)_p$ determined from V_m^E is useful to gain insights into the interactional and structural features of the systems under consideration. Its sign is the result of the variation in the balance of association/solvation and structural effects with temperature, and depends on the size and shape of the component molecules [56]. For systems with short 1-alkanol and long n-alkane, A_p is positive over the whole concentration range (association effects are dominant). For mixtures of long 1-alkanol and a short n-alkane, A_p shows negative values in the concentration region where interstitial accommodation is important [56–58]. In the case of linear polyether + alkane mixtures, A_p is usually positive and decrease with the size of the oxaalkane in such way that for the 2,5,8,11,14-pentaoxapentadecane

+ heptane or + cyclohexane systems becomes negative [59] as consequence of dominant structural effects. For the present systems, and at the compositions where the curves have their minimum value, we have: A_p/cm^3·mol^{-1}·K^{-1} = $-7.6·10^{-4}$ ($n = 2$; $x_1 = 0.5993$); $-1.23·10^{-3}$ ($n = 3$; $x_1 = 0.5962$); $-2.1·10^{-3}$ ($n = 4$; $x_1 = 0.6966$). This confirms the existence of structural effects in the present solutions. The negative A_p (303.15 K) value of the 1-propanol + PEG-250 mixture (-0.001 cm^3·mol^{-1}·K^{-1} [60]) is in agreement with our statement. In systems with 2,5-dioxahexane, the change from a positive A_p value for the ethanol mixture ($A_p = 2.4·10^{-3}$ cm^3·mol^{-1}·K^{-1}) to a negative value for the 1-octanol solution ($-3.2·10^{-3}$ cm^3·mol^{-1}·K^{-1} [61]) reveals that association effects are dominant in the former mixture, while structural effects are determinant in the latter. It is also interesting to compare A_p results for methanol + 2,5,8-trioxanonane, or + 3,6,9-trioxaundecane ($2·10^{-3}$ cm^3·mol^{-1}·K^{-1} [62]) systems. Such difference in the sign newly reveals that association effects are more important in the 3,6,9-trioxaundecane solution, since the O atoms are more sterically hindered in this polyether and interactions between unlike molecules are more difficult to be stated.

5.3. Viscosimetric data

The $\Delta\eta$ values listed in Table 3 show that they are positive and that increase with the number of CH$_2$CH$_2$O groups of the oxaalkane: 0.068 ($n = 2$) < 0.195 ($n = 3$) < 0.349 ($n = 4$), all values in mPa·s. These positive $\Delta\eta$ values reveal that there is a loss of fluidization of the system along mixing, usually ascribed to the existence of strong interactions between unlike molecules [63]. For example, $\Delta\eta$/mPa·s = 0.132 for methanol + 1-propylamine [64], 0.20 for methanol + 1-butylamine [65], and 0.18 for CHCl$_3$ + N,N,N-triethylamine (TEA) [66]. For the cited solutions, their H_m^E values largely differ from the result given above for methanol + polyether systems. Thus, H_m^E/J·mol^{-1} = -3794 for methanol + 1-propylamine [67], -3767 for methanol + 1-butylamine [67], and -4072 for CHCl$_3$ + TEA [68]. Negative $\Delta\eta$ values are commonly interpreted in terms of a higher fluidization of the system caused by the disruption of interactions between like molecules [69], which overcompensates the increase of $\Delta\eta$ related to the creation of interactions between unlike molecules upon mixing [38]. This trend is clearly observed for 1-alkanol + alkane or + amine mixtures [38, 69–71]. However, viscosity is a very sensitive magnitude to size effects and our results should be ascribed to the existence of strong structural effects in the investigated solutions. In fact, mixtures characterized by strong interactions between unlike molecules and positive $\Delta\eta$ results may show $\eta(x_1)$ curves with a maximum [63], a behaviour not observed for the treated solutions (Figure 3.1).

Finally, it should be mentioned that using the value $\Delta\eta = -0.036$ mPa·s for the methanol + 2,5-dioxahexane mixture [72], we find a good correlation between $\Delta\eta$ and the difference in volume between the mixture components, $V_{m1} - V_{m2}$, for methanol + CH$_3$−O−(CH$_2$CH$_2$O)$_n$−CH$_3$ systems. Thus, $\Delta\eta = (-0.255$ mPa·s$) + (0.0033$ mPa·s/cm^3·mol^{-1})$(V_{m1} - V_{m2})$, with $r = 0.994$ and the standard deviation equal to 0.015 mPa·s.

It is known that the application of the Grunberg-Nissan equation to the correlation of viscosity data leads to the determination of small and negative G_{12} values for mixtures which show positive deviations from the Raoult's law. In contrast, positive G_{12} values are obtained for systems characterized by negative deviations from the Raoult's law [63, 66]. In our case, $G_{12} = 0.515$ ($n = 2$), 1.280 ($n = 3$) and 1.972 ($n = 4$) (Table 5). 1-Alkanol + polyether mixtures show positive deviations from the Raoul's law as it is indicated by the corresponding values of the molar

Table 6
Enthalpies, ΔH^*, entropies, ΔS^*, Gibbs energies, ΔG^*, and deviations of Gibbs energies, $\Delta(\Delta G^*)$, of activation of viscous flow for the methanol (x_1) + polyether $(1 - x_1)$ systems at 298.15 K.

x_1	$\Delta H^*/\text{J·mol}^{-1}$	$\Delta S^*/\text{J·mol}^{-1}\cdot\text{K}^{-1}$	$\Delta G^*/\text{J·mol}^{-1}$	$\Delta(\Delta G^*)/\text{J·mol}^{-1}$
		Methanol (x_1) + 2,5,8-trioxanonane $(1 - x_1)$		
0	11362	−10.7	14563	0
0.0560	11326	−10.4	14426	120
0.1076	11354	−9.9	14292	223
0.2020	11231	−9.4	14021	386
0.2929	11316	−8.2	13757	540
0.3965	11191	−7.5	13414	672
0.4979	10999	−6.8	13036	760
0.5993	10987	−5.4	12608	798
0.6891	11040	−3.8	12167	769
0.7967	10506	−3.5	11558	654
0.8412	10526	−2.5	11267	567
0.8996	10455	−1.3	10840	409
0.9480	10534	0.3	10453	244
1	10495	1.8	9971	0
		Methanol (x_1) + 2,5,8,11-tetraoxadodecane $(1 - x_1)$		
0	14631	−7.5	16852	0
0.0543	14471	−7.4	16679	200
0.0988	14475	−6.9	16534	362
0.1978	14129	−6.9	16197	706
0.3013	14021	−6.0	15797	1018
0.3994	13448	−6.4	15369	1265
0.5183	13084	−5.6	14766	1480
0.5962	12681	−5.4	14296	1547
0.6983	12141	−4.8	13571	1524
0.7969	11454	−4.1	12688	1320
0.8472	11102	−3.5	12154	1132
0.8993	10827	−2.3	11517	854
0.9489	10724	−0.3	10820	498
1	10495	1.8	9971	0
		Methanol (x_1) + 2,5,8,11,14-pentaoxapentadecane $(1 - x_1)$		
0	17502	−3.9	18669	0
0.0463	17419	−3.7	18513	247
0.1031	17036	−4.3	18321	549
0.1978	16766	−4.0	17960	1011

Table 6
(Continuation.)

x_1	$\Delta H^*/\text{J·mol}^{-1}$	$\Delta S^*/\text{J·mol}^{-1}\text{·K}^{-1}$	$\Delta G^*/\text{J·mol}^{-1}$	$\Delta(\Delta G^*)/\text{J·mol}^{-1}$
0.3111	16152	−4.4	17469	1506
0.3886	15835	−4.2	17075	1786
0.4940	15242	−4.1	16453	2080
0.5935	14586	−3.9	15748	2242
0.6966	13649	−4.1	14857	2247
0.7966	12583	−3.9	13756	2016
0.8472	11924	−3.8	13046	1747
0.8972	11173	−3.5	12230	1366
0.9495	11152	−0.2	11204	794
1	10495	1.8	9971	0

excess Gibbs energies, G_{m}^{E}. Thus, at 308.15 K, G_{m}^{E}(2,5,8-trioxanonane)/J·mol^{-1} = 283 (methanol), 313 (1-propanol) [73]. In consequence, the present G_{12} results should be ascribed to the existence of strong structural effects. Note that newly, there is a good linear dependence of G_{12} with $V_{\text{m1}} - V_{\text{m2}}$ since $G_{12} = -1.377 + (0.019 \text{ cm}^{-3}\text{.mol})(V_{\text{m1}} - V_{\text{m2}})$, with $r = 0.999$. Similar results have been obtained for other systems with compounds which differ largely in size. For example, $G_{12} = 1.95$ for the 1-decanol + 1-propylamine mixture at 303.15 K [74].

As usually, $\Delta\eta$ decreases when the temperature is increased (Table 3). The density and viscosity data may be used to determine the Gibbs energy of activation of viscous flow, ΔG^*, in the framework Eyring's theory [75–77]. The enthalpy, ΔH^*, and the entropy, ΔS^*, of activation of viscous flow may be obtained at different temperatures from [18, 78]:

$$\ln \frac{\eta V_{\text{m}}}{h N_{\text{A}}} = \frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} \tag{22}$$

The plots of $\ln\left(\eta V_m/h N_{\text{A}}\right)$ against $1/T$ give a straight line for each mixture. The magnitudes ΔH^* and ΔS^* can be then estimated from its slope and intercept. Values for ΔH^*, ΔS^* and the corresponding excess properties are listed in Table 6.

Data reveal that the entropy change of activation from the initial state to the transition state at a given composition is rather small during the activated viscous flow process and that ΔG^* is essentially determined by enthalpic effects. On the other hand, ΔH^* increases with the number of CH_2CH_2O groups in the oxaalkane, i.e., when the solvent is more structured, as dipolar interactions are more relevant in the pentaether system than in the triether solution. This is supported by the relative variation of H_{m}^{E} values and of UCSTs of $CH_3-O-(CH_2CH_2O)_n-CH_3 + n$-alkane systems (280.81 K for 2,5,8,11-tetraoxadodecane + dodecane mixtures [79] and 281.8 K for 2,5,8,11,14-pentaoxapentadecane + octane mixtures [80]). In addition, it is remarkable that ΔS^* of pure oxaalkane become less negative when its chain length increases (Table 6). We have also determined $\Delta(\Delta G^*)$ ($= \Delta G^* - x_1\Delta G_1^* - x_2\Delta G_2^*$) at 298.15 K (Figure 3.2).
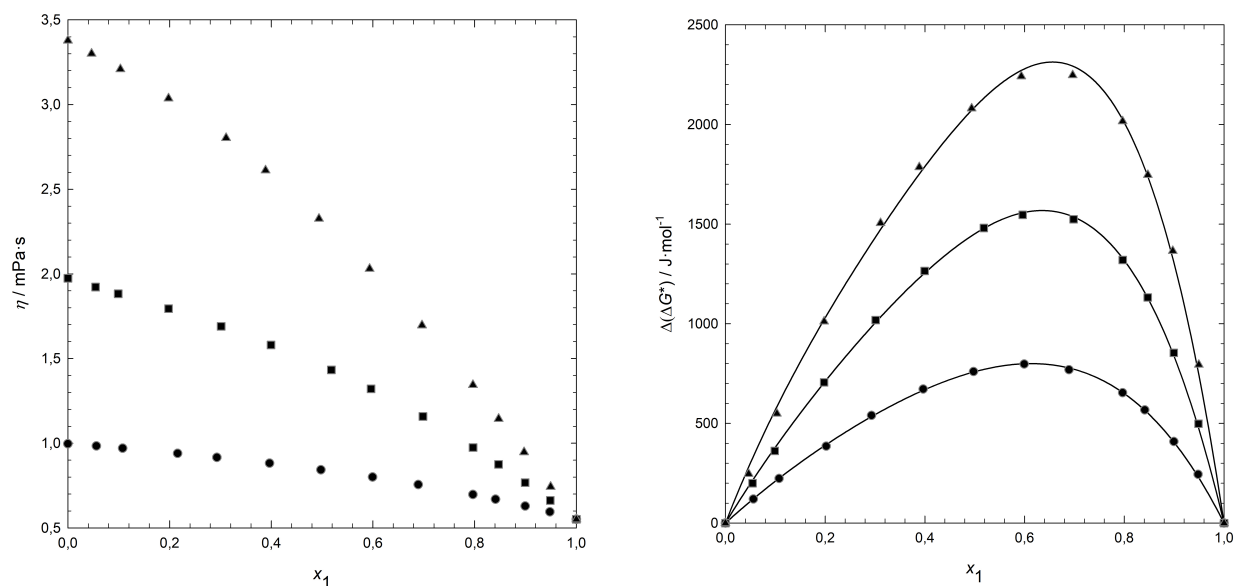
Figure 3: (1) Dynamic viscosities, η, and (2) deviations of Gibbs energies of activation of viscous flow, $\Delta(\Delta G^*)$, for methanol (x_1) + n-polyether $(1 - x_1)$ mixtures at 298.15 K and atmospheric pressure. Solid lines, results from the smoothing Eq. (13) with the coefficients listed in Table 4. Points, experimental data: ● 2,5,8-trioxanonane; ■ 2,5,8,11-tetraoxadodecane; ▲ 2,5,8,11,14-pentaoxapentadecane.

The $\Delta(\Delta G^*)$/J·mol^{-1} variation is as follows: 759 ($n = 2$) < 1465 ($n = 3$) < 2086 ($n = 4$), and also changes linearly with $V_{m1} - V_{m2}$. Large positive values of $\Delta(\Delta G^*)$ have been also encountered for mixtures with compounds very different in size, as for the already mentioned system 1-decanol + 1-propylamine at 303.15 K (= 1478 J·mol^{-1}) [74].

6. Conclusions

Data on V_m^E and $\Delta\eta$ at various temperatures and atmospheric pressure for methanol + n-polyether systems are reported. The large and negative V_m^E values can be explained in terms of positive contributions due to breaking of like interactions of the pure liquids and negative contributions due to the formation of unlike interactions and structural effects. A further study of the data allows us to conclude that the negative V_m^E is mainly due to the close packing effect. Since our ethers are bulkier in size, they can accommodate methanol molecules in the voids. Therefore, for systems comprising longer ethers, free volume contributions are relatively more important and larger negative V_m^E values are observed. The positive $\Delta\eta$ values of the methanol + n-polyether mixtures indicate that there are interaction between unlike molecules. However, the viscosity measurements and the results obtained from the correlation of the data using the Grunberg-Nissan equation indicates a predominant contribution of structural effects on interactional effects, which become more important for large n values.

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