



Density and excess molar enthalpy of (2-propanol + glyme) liquid mixtures. Application of the Flory model

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ABSTRACT

For glymes of general formula $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_u\text{CH}_3$, with $u = 1, 2, 3, 4$, the densities of the (2-propanol + glyme) systems at temperatures ranging from (293.15 to 303.15) K and at pressure 0.1 MPa were determined using a DSA 5000 densimeter (from Anton Paar). The corresponding excess molar volumes were calculated from these density measurements. In addition, excess molar enthalpies at 298.15 K and 0.1 MPa were measured using a Tian-Calvet micro-calorimeter. The results show that alkanol-ether interactions are strong but do not contribute significantly to the excess molar enthalpy, as the values are large and positive, and comparable to those of (glyme + *n*-heptane) systems. The excess molar volumes are small or even negative (in the case of the mixture with $u = 4$), indicating that they are mainly governed by structural effects. Mixtures with 1-propanol or 2-propanol behave similarly, although interactions between unlike molecules become slightly stronger when 1-propanol is involved. On the other hand, effects related to alcohol self-association play a decisive role in the thermodynamic properties when glymes are replaced by di-*n*-propyl ether. This is supported by the application of the Flory model, which shows that orientational effects are weak in the studied glyme-containing mixtures but become significantly stronger when di-*n*-propyl ether is considered.

1. Introduction

The study of (alkanol + ether) mixtures has attracted significant interest due to their wide range of applications. These systems are commonly used as gasoline additives, increasing the octane rating and reducing emissions [1,2]. Solutions comprising an alkanol as a refrigerant and a polyether as an absorbent have been proposed as effective working fluids in absorption heat pumps [3]. (Alkanol + ether) systems are also relevant in other industrial processes, particularly because alkanols serve as fundamental components in the synthesis of oxalanes and are therefore often present as impurities in such processes. Moreover, mixtures of short-chain alkanols with linear polyethers are useful as simplified models for the complex (water + polyethylene glycols) systems, which are extensively used in biochemical and biomedical applications [4]. These solutions, especially those involving cyclic ethers, are also gaining attention in biotechnology [5,6].

From a theoretical perspective, the investigation of (alkanol + ether) mixtures is crucial due to the complex interactional and structural effects involved. In this context, when studying such systems, one must

consider the self-association of alkanols and the dipolar interactions between ether molecules, both of which are disrupted upon mixing, as well as the formation of new alkanol-ether interactions during the mixing process. The presence of multiple oxygen atoms within the same ether molecule introduces an additional problem due to the so-called proximity effects, which arise from dipolar interactions between these atoms [7–9]. Consequently, the analysis of this class of solutions serves as a rigorous test for any theoretical model [9]. Furthermore, it also provides a useful preliminary step toward studying mixtures containing hydroxyethers, where intramolecular effects between the –OH and –O– groups within the same molecule become significant [10].

Our research group has extensive experience in the investigation of systems containing –OH and/or –O– groups, either within the same molecule or in different ones. In particular, we have focused on (1-alkanol + linear monoether [8,11], or + polyether [12–14] or + cyclic ether [7,11]) mixtures or to systems involving hydroxyethers [10]. As a continuation of these works, and as a contribution to the Thermodynamics of Organic Mixtures (TOM) project [15–17], we now report density measurements, ρ , of the (2-propanol + linear polyether)

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mixtures at temperatures $T = (293.15 \text{ to } 303.15) \text{ K}$ and pressure $p = 0.1 \text{ MPa}$. The linear polyethers considered follow the general formula $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_u\text{CH}_3$, with $u = 1, 2, 3, 4$, referred to as mono, di, tri, and tetra-glyme, respectively. The results were used to calculate the corresponding excess molar volumes, V_m^E . In addition, calorimetric measurements of the excess molar enthalpy, H_m^E , were performed at $T = 298.15 \text{ K}$ and $p = 0.1 \text{ MPa}$ for the same systems. This set of data is essential to achieve the objective of this work: to provide insight into the interactional and structural changes occurring in these mixtures, and to analyze the effect on the mixture properties of replacing a primary alkanol with a secondary one, namely, 1-propanol with 2-propanol, while maintaining the same number of carbon atoms.

2. Materials and methods

2.1. Materials

The liquids used in this study are listed in Table 1, along with their source and purity.

Table 2 shows the measured properties of the pure compounds at a pressure of $p = 0.1 \text{ MPa}$: density, ρ , at temperatures $T = (293.15 \text{ to } 303.15) \text{ K}$, and the isobaric thermal expansion coefficient, α_p , at $T = 298.15 \text{ K}$. The values α_p have been obtained using the following equation:

$$\alpha_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \quad (1)$$

where ρ is the density at $T = 298.15 \text{ K}$, and $(\partial \rho / \partial T)_p$ is calculated as the slope of the linear regression of ρ as a function of T in the range $T = (293.15 \text{ to } 303.15) \text{ K}$. The comparison between the measured and literature values is satisfactory. For subsequent calculations, the literature values of the isothermal compressibilities, κ_T , of the pure compounds at $T = 298.15 \text{ K}$ are also included in Table 2.

2.2. Apparatus and procedure

Density data were determined using a vibrating-tube densimeter (DSA 5000, Anton Paar). The temperature of the apparatus is controlled by Peltier modules and a Pt-100 resistance thermometer, achieving a stability of 0.001 K . Further details on the technique are described elsewhere [38,39].

The calibration of the DSA 5000 was performed by fitting the density values, ρ , of reference liquids, obtained from the literature, to the well-established characteristic equation of vibrating-tube densimeters:

$$\rho = A + B Q^2 \quad (2)$$

where Q denotes the ratio between the resonance period of the measuring tube and that of the reference tube, and parameters A and B

Table 1
Description of the compounds used in this work.

Chemical name	CAS Number	Source	^a Initial purity	Purification method
2-propanol	67–63–0	Sigma-Aldrich	0.9995	none
2,5-dioxahexane (monoglyme)	110–71–4	Sigma-Aldrich	0.999	none
2,5,8-trioxanonane (diglyme)	111–96–6	Fluka	0.998	none
2,5,8,11-tetraoxadodecane (triglyme)	112–49–2	Sigma-Aldrich	0.999	none
2,5,8,11,14-pentaoxapentadecane (tetraglyme)	143–24–8	Sigma-Aldrich	0.999	none

^a Gas chromatography area fraction. Certified by the supplier.

are determined at each temperature at which the mixtures are to be measured, using the following series of pure liquids: *n*-heptane, isooctane, cyclohexane, toluene, and Milli-Q water. Viscosity corrections have been neglected, since the viscosities of the liquids used are low. The estimated contribution to the uncertainty of density from the calibration parameters A and B is $<0.00010 \text{ g cm}^{-3}$. However, the overall measurement uncertainty of the densimeter is higher and is evaluated as detailed in Section 2.4.

The possible contamination and stability of the pure liquids used in this work were monitored periodically by measuring their densities, which remained within a maximum deviation of $2 \cdot 10^{-5} \text{ g cm}^{-3}$ from the initial values. The liquid mixtures were prepared by weighing, using an analytical balance (MSU125P, Sartorius), and applying the corresponding correction for buoyancy effects. This procedure resulted in a standard uncertainty of $5 \cdot 10^{-5} \text{ g}$. The calculated concentration is expressed as the mole fraction of 2-propanol, x_1 , throughout the remainder of the text, unless otherwise indicated.

Calorimetric data were obtained by means of a standard Tian-Calvet microcalorimeter with a temperature stability of 0.01 K . The calorimetric block consists of two wells equipped with thermopiles connected in a differential configuration. One well contains the liquid sample under study (L), while the other holds the reference sample (R).

The instrument was calibrated electrically by supplying a constant power to the sample well until the calorimeter reached a steady state, while measuring the differential electromotive force (emf) at the microcalorimeter output. The calibration constant, C , was determined using the following equation:

$$C = \frac{\frac{\delta Q_L}{dt} - \frac{\delta Q_R}{dt}}{\varepsilon_{\text{diff}}} = \frac{P}{\varepsilon_{\text{diff}}} \quad (3)$$

where $\frac{\delta Q_L}{dt} - \frac{\delta Q_R}{dt}$ represents the difference between the heat flow from the sample and reference wells, P is the power generated in the sample well (calculated as the product of the voltage and current applied to it), and $\varepsilon_{\text{diff}}$ is the differential emf.

The calibration setup consists of: (i) Two metallic calibration cells, each containing a wound manganin wire resistor. A power supply (6644A, Agilent) controls both the power supplied to the calibration cell located in the sample well and the duration of the power supply. (ii) A thermal power monitoring module, comprising a multimeter (PM2534, Philips) for measuring the voltage across the resistor, and a multimeter (34410A, Agilent) for measuring the current through the resistor. (iii) A multimeter (2000, Keithley) for monitoring the output voltage generated by the thermopiles; this device is, in fact, the only one required to determine H_m^E once the calorimeter has been calibrated.

The calibration procedure is carried out at different supply currents ranging from 5 mA to 35 mA , maintaining each current level stable for approximately 4 h . The estimated relative standard uncertainty in the calibration constant C is 0.1% . However, the overall measurement uncertainty increases by an order of magnitude due to factors such as calorimeter signal integration. The total uncertainty in H_m^E is determined as described in Section 2.4.

The measurement of the H_m^E of the two liquids was conducted as follows. Custom-made stainless steel mixing cells, with a total volume of approximately 9 cm^3 , were used. Prior to mixing, one liquid was placed in the cell, and the other one in a syringe, both housed within the calorimetric block, until thermal equilibrium was reached. The $\varepsilon_{\text{diff}}$ was then recorded for 10 min (baseline) and averaged. Subsequently, the liquid in the syringe was slowly and continuously injected into the cell, producing a signal peak due to mixing. After thermal equilibrium was re-established, the baseline was recorded for 10 min and averaged to check that this baseline has not significantly changed and that it is stable enough to ensure that no other thermal effects are influencing the signal. The total heat released by the mixture was determined by multiplying the calibration constant C by the integral of $\varepsilon_{\text{diff}}$ over the time interval during which the mixture absorbed or released heat. The reference level

Table 2

Density, ρ , isobaric thermal expansion coefficient, α_p , and isothermal compressibility, κ_T , of the pure liquids used in this work at temperature T and pressure $p = 0.1$ MPa. Root-mean-square deviation, $\sigma(F)$, of the literature values from the experimental values at temperature $T = 298.15$ K (see Eq. (6)).

Compound	^a Property F	This work			Literature	
		$T = 293.15$ K	$T = 298.15$ K	$T = 303.15$ K	$T = 298.15$ K	^a $\sigma(F)$
2-propanol	$\rho/(\text{g cm}^{-3})$	0.78505	0.78085	0.77660	0.7809 [18] 0.7809 [19] ^b 0.78087 [20] 0.7809 [21] 0.78087 [22]	0.000045
	$\alpha_p/(10^{-3} \text{ K}^{-1})$		1.082		1.09 [18] 1.084 [19] ^b 1.085 [20] 1.075 [21] ^b 1.086 [22]	0.0060
monoglyme	$\kappa_T/(\text{TPa})^{-1}$ $\rho/(\text{g cm}^{-3})$	0.86717	0.86170	0.85621	1110 [21] 0.86183 [23] 0.86114 [24] 0.86114 [25] 0.86110 [26] 0.8616 [27] 0.86208 [28]	0.00048
	$\alpha_p/(10^{-3} \text{ K}^{-1})$		1.272		1.269 [23] ^b 1.277 [24] ^b 1.274 [25] ^b 1.29 [26]	0.011
diglyme	$\kappa_T/(\text{TPa})^{-1}$ $\rho/(\text{g cm}^{-3})$	0.94370	0.93874	0.93376	1114.5 [27] 0.93872 [23] 0.93935 [24] 0.93883 [25] 0.93859 [26] 0.9384 [29] 0.93882 [30]	0.00032
	$\alpha_p/(10^{-3} \text{ K}^{-1})$		1.059		1.063 [23] 1.064 [24] 1.057 [25] 1.055 [26] 821.6 [27]	0.0045
triglyme	$\kappa_T/(\text{TPa})^{-1}$ $\rho/(\text{g cm}^{-3})$	0.98485	0.98010	0.97535	0.98079 [23] 0.98058 [24] 0.98049 [31] 0.9805 [32] 0.98064 [33] 0.98000 [34]	0.00051
	$\alpha_p/(10^{-3} \text{ K}^{-1})$		0.969		0.969 [23] 0.969 [24] ^b 0.969 [31] ^b 0.964 [32] ^b 0.969 [33]	0.0025
tetraglyme	$\kappa_T/(\text{TPa})^{-1}$ $\rho/(\text{g cm}^{-3})$	1.01090	1.00626	1.00164	707.1 [27] 1.00569 [23] 1.00668 [24] 1.00716 [35] 1.00568 [36] 1.0066 [34]	0.00066
	$\alpha_p/(10^{-3} \text{ K}^{-1})$		0.920		0.925 [23] 0.928 [24] ^b 0.915 [35] ^b 0.929 [36]	0.0081
	$\kappa_T/(\text{TPa})^{-1}$				644.0 [37]	

^a Expanded uncertainties (U_1), with a coverage factor of 2, evaluated under repeatability conditions of measurement: $U_1(T) = 0.02$ K, $U_1(p) = 10$ kPa, and $U_1(\rho) = 0.00010$ g cm⁻³, $U_1(\alpha_p) = 0.020 \cdot 10^{-3}$ K⁻¹. Expanded uncertainties (U_2), with a coverage factor of 2, evaluated under reproducibility conditions of measurement: for $F = \rho, \alpha_p, U_2(F) = 2\sigma(F)$. Total expanded uncertainty (U): $U(F) = [U_1(F)^2 + U_2(F)^2]^{1/2}$.

^b Calculated from data reported in the reference.

for the integration in the $\varepsilon_{\text{diff}}$ vs. time representation was taken as a straight line connecting the initial and final baselines. Further details on the technique are provided in previous works [38,39].

2.3. Excess functions

The values F^{id} of the thermodynamic properties of an ideal mixture, under the same temperature and pressure conditions as the real mixture, are calculated using the Benson and Kiyohara formulas [40–42]:

$$F^{\text{id}} = x_1 F_1 + x_2 F_2 \quad (F = V_m, H_m, (\partial V_m^E / \partial T)_{p,x}) \quad (4)$$

$$F^{\text{id}} = \phi_1 F_1 + \phi_2 F_2 \quad (F = \alpha_p, \kappa_T) \quad (5)$$

where F_i is the value of the property F for pure component i , x_i represents the mole fraction of component i , and $\phi_i = x_i V_{m,i} / V_m^{\text{id}}$ is the volume fraction of component i . The excess properties F^E are defined as:

$$F^E = F - F^{\text{id}} \quad (6)$$

In the case of $F = H_m$, the excess molar enthalpy H_m^E is equal to the molar heat of mixing at constant pressure, measured directly by calorimetry.

Interactional effects upon mixing are better evaluated by means of the isochoric excess molar internal energy, $U_{m,V}^E$ [43]:

$$U_{m,V}^E = H_m^E - T \frac{\alpha_p}{\kappa_T} V_m^E \quad (7)$$

In Eq. (7), the term $T(\alpha_p / \kappa_T) V_m^E$ is referred to as the equation-of-state term (EoS term), and it is related to the volume variation upon mixing. Due to the lack of κ_T values for the mixtures studied in this work, $U_{m,V}^E$ has been estimated by assuming ideal behavior for this quantity, using literature κ_T values (see Table 2) and Eq. (5).

2.4. Experimental uncertainty

Details regarding the uncertainty of some of the measurements have already been published in a previous work [44], but they are fully specified below.

Uncertainty under repeatability conditions. This term refers to the uncertainty obtained from the sample standard deviation of measurements performed while maintaining the same procedure, operator, measuring system, operating conditions, location, and source liquids over short time intervals and includes the contribution from calibration constants. It is denoted (with a coverage factor of 2) as U_1 [45]. The highest values found in this study are: $U_1(T) = 0.02$ K, $U_1(p) = 10$ kPa, $U_1(x_1) = 0.00010$, $U_1(\rho) = 0.00010$ g cm⁻³, $U_1(\alpha_p) = 0.020 \cdot 10^{-3}$ K⁻¹, $U_1(H_m^E) = 0.010 \cdot |H_m^E|$.

Uncertainty under reproducibility conditions. This is based on the expression of the root-mean-square deviation, $\sigma(F)$, of N_{lit} literature (lit) data points from our experimental (exp) values:

$$\sigma(F) = \left[\frac{1}{N_{\text{lit}} - 1} \sum_{F_{\text{lit}}} (F_{\text{lit}} - F_{\text{exp}})^2 \right]^{1/2} \quad (F = \rho, \alpha_p) \quad (8)$$

The summation is performed over each literature data point F_{lit} at $T = 298.15$ K. For pure liquids, the expanded (with a coverage factor of 2) uncertainty evaluated under reproducibility conditions, U_2 , is estimated as $U_2(F) = 2 \sigma(F)$. For mixtures, $U_2(F)$ is taken as the maximum value between those corresponding of the pure liquids involved (Table 2).

Total expanded (with a coverage factor of 2) uncertainty, U . Ideally, this should include other factors, such as the purity of the compounds used. However, these are very difficult to quantify. Therefore, for the mole fraction of the mixtures, the total expanded uncertainty has been roughly estimated as $U(x_1) = 0.0010$. For $F = \rho, \alpha_p$, the total expanded uncertainty can be calculated as:

$$U(F) = [U_1(F)^2 + U_2(F)^2]^{1/2} \quad (F = \rho, \alpha_p) \quad (9)$$

Specifically, for the mixtures of 2-propanol with monoglyme, diglyme, triglyme, and tetraglyme, the uncertainty in density, $U(\rho)$, is 0.00097 g cm⁻³, 0.00065 g cm⁻³, 0.0010 g cm⁻³, and 0.0013 g cm⁻³, respectively.

The uncertainties of the excess functions are considerably less sensitive to the purity of the compounds and are typically estimated by comparison with reference values from test systems. The following expressions are used: $U(V_m^E) = 0.010 |V_m^E|_{\text{max}} + 0.005$ cm³ mol⁻¹, $U_r(H_m^E) = 0.015$, and $U[(\partial V_m^E / \partial T)_{p,x}] = 0.010 |(\partial V_m^E / \partial T)_{p,x}|_{\text{max}} + 0.0002$ cm³ mol⁻¹ K⁻¹.

3. Results

The experimental ρ and V_m^E values for (2-propanol + linear polyether) liquid mixtures at $p = 0.1$ MPa and $T = (293.15 \text{ to } 303.15)$ K are included in Table 3 as functions of x_1 . The values of $(\partial V_m^E / \partial T)_{p,x}$ at $p = 0.1$ MPa and $T = 298.15$ K are also included in Table 3, calculated as the slope of linear regressions of V_m^E as a function of T in the range $T = (293.15 \text{ to } 303.15)$ K. The experimental values of H_m^E at $p = 0.1$ MPa and $T = 298.15$ K are collected in Table 4.

Some excess properties, $F^E = V_m^E, H_m^E, (\partial V_m^E / \partial T)_{p,x}$, are fitted to Redlich-Kister polynomials [46]:

$$F^E = x_1(1 - x_1) \sum_{i=0}^{k-1} A_i (2x_1 - 1)^i \quad (F^E = V_m^E, H_m^E, (\partial V_m^E / \partial T)_{p,x}) \quad (10)$$

using unweighted linear least-squares regressions, selecting an appropriate number, k , of A_i coefficients based on F-tests for the inclusion of additional terms [47]. The results are presented in Table 5. The root-mean-square deviation of the fit to Eq. (10), s , is defined as:

$$s = \left[\frac{1}{N - N_p} \sum_{j=1}^N (F_{\text{cal},j} - F_{\text{exp},j})^2 \right]^{1/2} \quad (F = V_m^E, H_m^E, (\partial V_m^E / \partial T)_{p,x}) \quad (11)$$

where N_p denotes the number of A_i parameters in Eq. (10), and j indexes the number N of experimental data points $F_{\text{exp},j}$ and the corresponding calculated values $F_{\text{cal},j}$. The value of s for each fit is included in Table 5.

The excess properties V_m^E, H_m^E , and $(\partial V_m^E / \partial T)_{p,x}$ of the studied mixtures at $p = 0.1$ MPa and $T = 298.15$ K are depicted as functions of x_1 in Figs. 1, 2, and 3, respectively, together with the corresponding Redlich-Kister regressions.

The interested reader may find in the Supplementary Material the excess partial molar volumes and enthalpies of both components of the (2-propanol + glyme) liquid mixtures studied (Tables S1 and S2, Figs. S1-S4), as well as the corresponding partial molar volumes (Table S1), at $T = 298.15$ K.

The V_m^E values obtained in this work have been compared with those reported in previous studies at atmospheric pressure [48–51], as illustrated in Fig. S5. Fig. S5a displays the V_m^E values for the (2-propanol + monoglyme) mixture at temperatures of 293.15 K and 303.15 K. Our data are consistent, within the experimental uncertainty, with those reported by [48] at both temperatures. In contrast, a significant discrepancy is observed when compared with the results of [51], particularly considering that their reported V_m^E values exhibit an inverse temperature dependence—decreasing with increasing temperature—which contradicts both our findings and those of [48].

Fig. S5b presents the V_m^E values for the (2-propanol + tetraglyme) mixture at $T = 298.15$ K. As shown, the density data reported by [49,50] lack the required precision to accurately determine the excess molar volumes, as they yield inconsistent values that fluctuate between positive and negative, and fail to exhibit the expected smooth compositional

Table 3

Density, ρ , excess molar volume, V_m^E , and temperature derivative of the excess molar volume, $(\partial V_m^E/\partial T)_{p,x}$ of (2-propanol (1) + linear polyether (2)) liquid mixtures as function of the mole fraction of 2-propanol, x_1 , at temperature T and pressure $p = 0.1$ MPa^a.

$\rho/(\text{g cm}^{-3})$			$V_m^E/(\text{cm}^3 \text{mol}^{-1})$			$(\partial V_m^E/\partial T)_{p,x}/(\text{cm}^3 \text{mol}^{-1} \text{K}^{-1})$
$T = 293.15$ K	$T = 298.15$ K	$T = 303.15$ K	$T = 293.15$ K	$T = 298.15$ K	$T = 303.15$ K	$T = 298.15$ K
2-propanol (1) + monoglyme (2)						
0.05178	0.86380	0.85836	0.0231	0.0260	0.0276	0.00045
0.10439	0.86021	0.85481	0.0548	0.0598	0.0658	0.00110
0.15427	0.85678	0.85141	0.0771	0.0850	0.0925	0.00154
0.20588	0.85310	0.84777	0.1039	0.1138	0.1246	0.00207
0.30275	0.84608	0.84084	0.1344	0.1466	0.1605	0.00261
0.40779	0.83815	0.83301	0.1531	0.1678	0.1828	0.00297
0.49539	0.83121	0.82617	0.1626	0.1780	0.1945	0.00319
0.60142	0.82245	0.81755	0.1586	0.1732	0.1884	0.00298
0.70143	0.81382	0.80907	0.1357	0.1482	0.1630	0.00273
0.79875	0.80491	0.80031	0.1090	0.1196	0.1302	0.00212
0.85010	0.80008	0.79558	0.0837	0.0915	0.0989	0.00152
0.89810	0.79539	0.79098	0.0619	0.0676	0.0737	0.00118
0.95061	0.79012	0.78582	0.0336	0.0360	0.0377	0.00041
2-propanol (1) + diglyme (2)						
0.05109	0.93918	0.93422	0.0075	0.0107	0.0108	0.00033
0.10475	0.93418	0.92922	0.0170	0.0237	0.0272	0.00102
0.15607	0.92913	0.92419	0.0289	0.0360	0.0399	0.00110
0.19889	0.92466	0.91973	0.0466	0.0552	0.0621	0.00155
0.29787	0.91373	0.90883	0.0630	0.0744	0.0852	0.00222
0.39453	0.90186	0.89700	0.0819	0.0951	0.1087	0.00268
0.49704	0.88786	0.88305	0.0915	0.1063	0.1199	0.00284
0.59926	0.87218	0.86744	0.0893	0.1040	0.1185	0.00292
0.70252	0.85426	0.84960	0.0712	0.0858	0.0986	0.00274
0.79283	0.83628	0.83173	0.0655	0.0769	0.0884	0.00229
0.84771	0.82438	0.81991	0.0379	0.0465	0.0560	0.00181
0.89995	0.81188	0.80750	0.0329	0.0382	0.0451	0.00122
0.94705	0.79980	0.79550	0.0175	0.0204	0.0247	0.00072
2-propanol (1) + triglyme (2)						
0.10260	0.97560	0.97085	0.0057	0.0094	0.0127	0.00070
0.16302	0.96960	0.96485	0.0069	0.0129	0.0181	0.00112
0.21067	0.96451	0.95977	0.0116	0.0177	0.0246	0.00130
0.30289	0.95374	0.94901	0.0138	0.0221	0.0306	0.00168
0.40500	0.94011	0.93540	0.0105	0.0202	0.0297	0.00192
0.49568	0.92607	0.92138	0.0145	0.0259	0.0364	0.00219
0.59697	0.90781	0.90315	0.0097	0.0225	0.0327	0.00230
0.68977	0.88795	0.88335	0.0074	0.0186	0.0279	0.00205
0.79723	0.86004	0.85553	0.0037	0.0128	0.0204	0.00167
0.84925	0.84410	0.83965	0.0009	0.0081	0.0146	0.00137
0.89995	0.82664	0.82226	-0.0010	0.0041	0.0081	0.00091
2-propanol (1) + tetraglyme (2)						
0.05776	1.00625	1.00162	-0.0146	-0.0157	-0.0129	0.00017
0.10331	1.00227	0.99763	-0.0164	-0.0144	-0.0109	0.00055
0.16636	0.99631	0.99168	-0.0162	-0.0148	-0.0104	0.00058
0.19980	0.99294	0.98830	-0.0199	-0.0157	-0.0128	0.00071
0.29568	0.98226	0.97763	-0.0291	-0.0245	-0.0181	0.00110
0.40048	0.96853	0.96390	-0.0412	-0.0337	-0.0271	0.00141
0.49985	0.95293	0.94832	-0.0513	-0.0439	-0.0366	0.00147
0.59618	0.93466	0.93008	-0.0628	-0.0561	-0.0489	0.00139
0.69890	0.91048	0.90594	-0.0688	-0.0623	-0.0565	0.00123
0.79196	0.88272	0.87824	-0.0658	-0.0606	-0.0558	0.00100
0.84810	0.86227	0.85784	-0.0573	-0.0530	-0.0499	0.00074
0.90240	0.83902	0.83466	-0.0474	-0.0453	-0.0438	0.00036
0.94957	0.81522	0.81093	-0.0287	-0.0277	-0.0271	0.00016

^a Total expanded uncertainties (U), with a coverage factor of 2: $U(T) = 0.02$ K, $U(p) = 10$ kPa, $U(x_1) = 0.0010$; $U(\rho)$ is estimated as $U_1(\rho) = 0.00010 \text{ g cm}^{-3}$ plus the maximum $U_2(\rho) = 2\sigma(\rho)$ value between those of the pure liquids involved (see Table 2), that is, $U(\rho) = [U_1(\rho)^2 + U_2(\rho)^2]^{1/2}$; $U(V_m^E) = 0.010 |V_m^E|_{\text{max}} + 0.005 \text{ cm}^3 \text{mol}^{-1}$; $U((\partial V_m^E/\partial T)_{p,x}) = 0.010 |(\partial V_m^E/\partial T)_{p,x}|_{\text{max}} + 0.0002 \text{ cm}^3 \text{mol}^{-1} \text{K}^{-1}$.

dependence.

4. Flory model

The essential hypotheses of the theory [52–54] are described elsewhere [55]. The basic assumption of the model is that of random mixing. The explicit expression of the Flory equation of state, valid for both pure liquids and liquid mixtures, is:

$$\frac{\hat{p}\hat{V}}{\hat{T}} = \frac{\hat{V}^{1/3}}{\hat{V}^{1/3} - 1} - \frac{1}{\hat{V}\hat{T}} \quad (12)$$

where $\hat{V} = V_m/V_m^*$, $\hat{p} = p/p^*$, and $\hat{T} = T/T^*$ stand for the reduced volume, pressure and temperature, respectively (where V_m is the molar volume of the mixture). For pure liquids, the reduction parameters, V_m^* , p^* , and T^* , can be obtained from values of density, $\alpha_{p,i}$ (isobaric expansion coefficient), and $\kappa_{T,i}$ (isothermal compressibility) (see

Table 4

Excess molar enthalpy, H_m^E , of (2-propanol (1) + linear polyether (2)) liquid mixtures as function of the mole fraction of 2-propanol, x_1 , at temperature $T = 298.15$ K and pressure $p = 0.1$ MPa ^a.

$H_m^E/(J\ mol^{-1})$ 2-propanol (1) + monoglyme (2)	x_1 2-propanol (1) + diglyme (2)	$H_m^E/(J\ mol^{-1})$ 2-propanol (1) + triglyme (2)	x_1 2-propanol (1) + tetraglyme (2)
0.05116	0.05862	0.04112	0.04079
0.10266	0.09944	0.10454	0.10101
0.14753	0.14873	0.15061	0.14880
0.20743	0.19941	0.19644	0.20190
0.31511	0.29935	0.29930	0.30358
0.39259	0.39978	0.40307	0.40874
0.50397	0.50348	0.50693	0.49262
0.60170	0.59184	0.59909	0.59730
0.71260	0.69626	0.69581	0.70215
0.79651	0.80243	0.80344	0.80673
0.85240	0.85192	0.85000	0.84681
0.89572	0.89319	0.89311	0.90341
0.93882	0.97297	0.95217	0.95277

^a Total expanded uncertainties (U) and relative expanded uncertainties (U_r) with a coverage factor of 2: $U(T) = 0.02$ K, $U(p) = 10$ kPa, $U(x_1) = 0.0010$, $U_r(H_m^E) = 0.015$.

Table 5

Parameters A_i of Eq. (10) and root-mean-square deviation of the fit, s , Eq. (11), for the excess molar volume, V_m^E , the temperature derivative of the excess molar volume, $(\partial V_m^E / \partial T)_{p,x}$, and the excess molar enthalpy, H_m^E , of (2-propanol (1) + linear polyether (2)) liquid mixtures used in this work at temperature T and pressure $p = 0.1$ MPa.

Property	T/K	A_0	A_1	A_2	A_3	s
2-propanol (1) + monoglyme (2)						
$V_m^E/(cm^3\ mol^{-1})$	293.15	0.644	0.05			0.003
	298.15	0.705	0.05			0.003
	303.15	0.769	0.05			0.003
$(\partial V_m^E / \partial T)_{p,x}/(cm^3\ mol^{-1}\ K^{-1})$	298.15	0.0125				0.00010
$H_m^E/(J\ mol^{-1})$	298.15	5292	97	410		3
2-propanol (1) + diglyme (2)						
$V_m^E/(cm^3\ mol^{-1})$	293.15	0.36	0.08	-0.15		0.004
	298.15	0.42	0.09	-0.14		0.004
	303.15	0.48	0.10	-0.16		0.004
$(\partial V_m^E / \partial T)_{p,x}/(cm^3\ mol^{-1}\ K^{-1})$	298.15	0.0117	0.0032			0.00008
$H_m^E/(J\ mol^{-1})$	298.15	6496	1165	604		13
2-propanol (1) + triglyme (2)						
$V_m^E/(cm^3\ mol^{-1})$	293.15	0.045	-0.037			0.0019
	298.15	0.092	-0.022			0.0019
	303.15	0.134	-0.016			0.0020
$(\partial V_m^E / \partial T)_{p,x}/(cm^3\ mol^{-1}\ K^{-1})$	298.15	0.0089	0.0021			0.00007
$H_m^E/(J\ mol^{-1})$	298.15	7383	1691	825	992	14
2-propanol (1) + tetraglyme (2)						
$V_m^E/(cm^3\ mol^{-1})$	293.15	-0.204	-0.23	-0.20		0.003
	298.15	-0.174	-0.22	-0.22		0.003
	303.15	-0.145	-0.22	-0.22		0.003
$(\partial V_m^E / \partial T)_{p,x}/(cm^3\ mol^{-1}\ K^{-1})$	298.15	0.0055				0.00011
$H_m^E/(J\ mol^{-1})$	298.15	7982	2233	1590	1715	11

Table 2). Expressions for the reduction parameters of mixtures can be found elsewhere [55]. The reduction parameters used in this work are listed in Table 6. The values of H_m^E are obtained from:

$$H_m^E = \frac{x_1 V_{m,1}^* \theta_2 X_{12}}{\hat{V}} + x_1 V_{m,1}^* P_1^* \left(\frac{1}{\hat{V}_1} - \frac{1}{\hat{V}} \right) + x_2 V_{m,2}^* P_2^* \left(\frac{1}{\hat{V}_2} - \frac{1}{\hat{V}} \right) \quad (13)$$

where all symbols have their usual meaning [55]. The reduced volume of the mixture, $\hat{V}$, is obtained from the equation of state, and the excess molar volume can be calculated as follows:

$$V_m^E = (x_1 V_{m,1}^* + x_2 V_{m,2}^*) (\hat{V} - \varphi_1 \hat{V}_1 - \varphi_2 \hat{V}_2) \quad (14)$$

4.1. Results from Flory's model

Table 6 lists the values of the interaction parameter X_{12} , determined

from experimental H_m^E data at equimolar composition and $T = 298.15$ K, using the method described in reference [57]. Deviations between experimental and theoretical H_m^E results (see Table 6 and Fig. 4 for a graphical comparison) are evaluated using the relative standard deviations of H_m^E , defined as:

$$\sigma_r(H_m^E) = \left[\frac{1}{N} \sum \left(\frac{H_{m,exp}^E - H_{m,calc}^E}{H_{m,exp}^E} \right)^2 \right]^{1/2} \quad (15)$$

where N is the number of experimental data points. Finally, experimental V_m^E results at $x_1 = 0.5$ and $T = 298.15$ K are also compared with the corresponding Flory calculations, as shown in Table 6.

5. Discussion

Unless otherwise indicated, the values of the thermophysical prop-

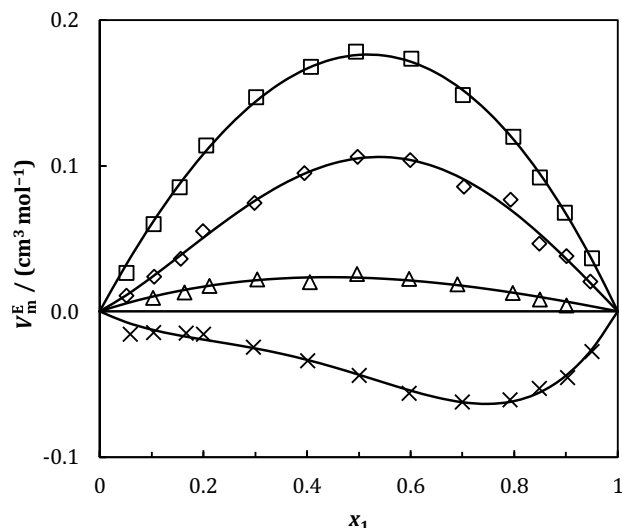


Fig. 1. Excess molar volume, V_m^E , of (2-propanol (1) + linear polyether (2)) liquid mixtures as a function of the 2-propanol mole fraction, x_1 , at temperature $T = 298.15$ K and pressure $p = 0.1$ MPa. Symbols, experimental values: ($\square$) monoglyme, ($\diamond$) diglyme, ($\triangle$) triglyme, ($\times$) tetraglyme. Solid lines are calculated with Eq. (10) using the coefficients from Table 5.

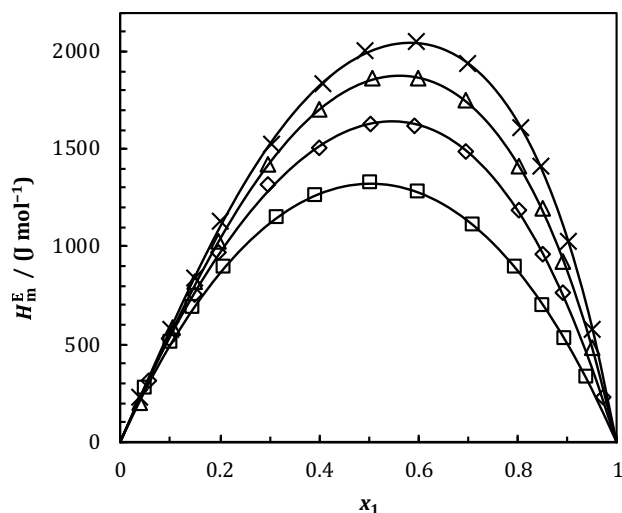


Fig. 2. Excess molar enthalpy, H_m^E , of (2-propanol (1) + linear polyether (2)) liquid mixtures as a function of the 2-propanol mole fraction, x_1 , at temperature $T = 298.15$ K and pressure $p = 0.1$ MPa. Symbols, experimental values: ($\square$) monoglyme, ($\diamond$) diglyme, ($\triangle$) triglyme, ($\times$) tetraglyme. Solid lines are calculated with Eq. (10) using the coefficients from Table 5.

erties are considered at $T = 298.15$ K, $p = 0.1$ MPa, and $x_1 = 0.5$ (see Tables 7 and 8, and Figs. 5 and 6) hereinafter. The number of carbon atoms in the n -alkane is denoted by n , and the number of oxygen atoms in the glyme is denoted by u .

5.1. (Alkanol + n -alkane) mixtures

Firstly, we focus on systems containing 1-alkanols. For mixtures with a fixed n -alkane (e.g., n -heptane), increasing the size of the 1-alkanol leads to an interesting behavior in both H_m^E and V_m^E . The (methanol + n -heptane) mixture exhibits a miscibility gap between 0.17 and 0.89 mole fraction of methanol at $T = 298.15$ K [70], due to the difficulty of the n -alkane in breaking the strong self-association of this alcohol. This

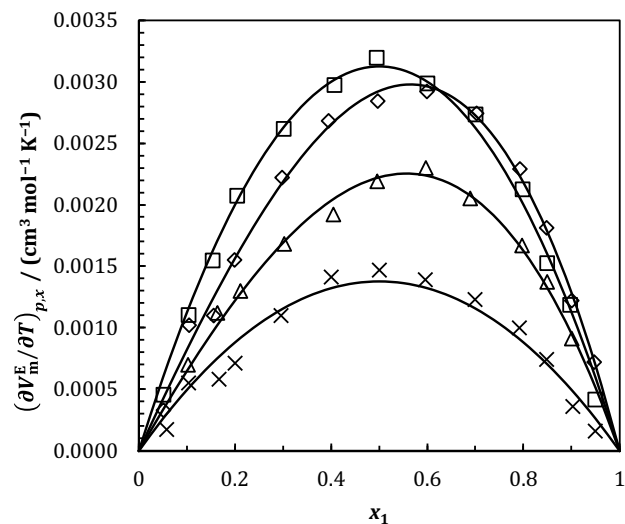


Fig. 3. Temperature derivative of the excess molar volume, $(\partial V_m^E / \partial T)_{p,x}$, of (2-propanol (1) + linear polyether (2)) liquid mixtures as a function of the 2-propanol mole fraction, x_1 , at temperature $T = 298.15$ K and pressure $p = 0.1$ MPa. Symbols, experimental values: ($\square$) monoglyme, ($\diamond$) diglyme, ($\triangle$) triglyme, ($\times$) tetraglyme. Solid lines are calculated with Eq. (10) using the coefficients from Table 5.

miscibility gap disappears at 298.15 K in n -heptane systems involving other 1-alkanols, as the $-\text{OH}$ group becomes more sterically hindered, leading to reduced self-association of the alkanol [63]. The H_m^E values are positive (arising from the disruption of interactions between alkanol molecules) and increase from ethanol to 1-propanol [71], but then gradually decrease [72]. This behavior is typically explained considering that, due to the lower self-association of longer 1-alkanols, the disruption of their intermolecular network upon mixing contributes less positively to H_m^E .

On the other hand, the sign of V_m^E depends on the size difference between the components of the mixture: V_m^E is positive for the shorter 1-alkanols and becomes negative starting from 1-hexanol. These negative values of V_m^E have been explained in terms of a purely structural effect known as interstitial accommodation [73,74].

Fixing 1-propanol as the 1-alkanol, the values of H_m^E for (1-propanol + n -alkane) mixtures increase slightly with the size of the n -alkane: $H_m^E / (\text{J mol}^{-1}) = 533$ (n -hexane [75]) < 614 (n -heptane [76]) < 685 (n -octane [77]), which can be attributed to the greater ability of longer alkanes to break interactions between 1-alkanol molecules. However, these small variations in H_m^E suggest that the self-associative structures of the alkanols are only slightly perturbed by the alkanes. Accordingly, the $H_m^E(x_1)$ curves are skewed toward low mole fractions of the 1-alkanol. The same trend is observed in the corresponding $V_m^E / (\text{cm}^3 \text{mol}^{-1})$ values: 0.180 (n -hexane [78]) < 0.295 (n -heptane [73]).

Let us now examine the effect of replacing 1-propanol with 2-propanol. As a starting point, it is important to note that the enthalpy of self-association of 2-propanol can be assumed to be equal to that of 1-alkanols. This approximation has been widely used in the application of association theories [63,79–82]. Nevertheless, the self-association of 2-propanol is lower than that of 1-propanol, since its $-\text{OH}$ group is more sterically hindered [63]. For mixtures with n -heptane, $H_m^E / (\text{J mol}^{-1}) = 614$ (1-propanol [76]) < 797 (2-propanol) [83]. This suggests that, in the case of 2-propanol mixtures, the breaking of dipolar interactions between alcohol molecules also contributes significantly to H_m^E . A similar behavior is observed in the corresponding $V_m^E / (\text{cm}^3 \text{mol}^{-1})$

Table 6

Results from the Flory model for (2-propanol (1) + ether (2)) mixtures at $p = 0.1$ MPa and $T = 298.15$ K: interaction parameter, X_{12} , relative standard deviations for H_m^E from Eq. (13), $\sigma_r(H_m^E)$, and excess molar volumes at equimolar composition, V_m^E . Flory parameters of pure compounds^a at $T = 298.15$ K are also included.

	$V_{m,i}/(\text{cm}^3 \text{mol}^{-1})$	$V_{m,i}^*/(\text{cm}^3 \text{mol}^{-1})$	$p_i^*/(\text{J cm}^{-3})$	N^b	$X_{12}/(\text{J cm}^{-3})$	$\sigma_r(H_m^E)$	$V_m^E/(\text{cm}^3 \text{mol}^{-1})$	
							Exp.	Flory
Monoglyme	104.58	80.39	575.9	13 ^c	75.53	0.051	0.176 ^c	1.257
Diglyme	142.93	113.47	609.8	13 ^c	84.65	0.029	0.105 ^c	1.140
Triglyme	181.84	146.59	626.1	13 ^c	90.76	0.056	0.023 ^c	1.024
Tetraglyme	220.89	179.43	645.5	13 ^c	94.18	0.041	−0.044 ^c	0.914
Dipropylether	137.68	106	440.7	14 ^d	50.63	0.273	−0.027 ^d	0.925

^a $V_{m,i}$, molar volume; $V_{m,i}^*$ and p_i^* , reduction molar volume and pressure, respectively. For 2-propanol: $V_{m,i} = 76.96 \text{ cm}^3 \text{mol}^{-1}$; $V_{m,i}^* = 60.87 \text{ cm}^3 \text{mol}^{-1}$; $p_i^* = 464.5 \text{ J cm}^{-3}$.

^b Number of data points.

^c This work.

^d Reference [56].

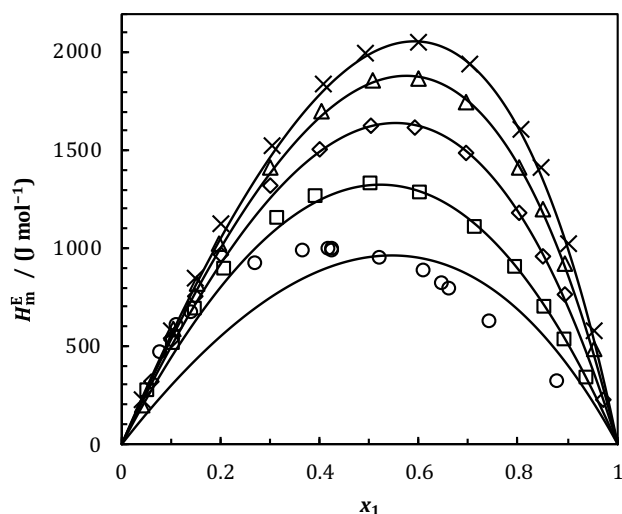


Fig. 4. Excess molar enthalpy, H_m^E , of (2-propanol (1) + linear polyether (2)) or + di-*n*-propyl ether (2)) liquid mixtures as a function of the 2-propanol mole fraction, x_1 , at temperature $T = 298.15$ K and pressure $p = 0.1$ MPa. Symbols, experimental values: (□) monoglyme [this work], (◇) diglyme [this work], (△) triglyme [this work], (×) tetraglyme [this work], (○) di-*n*-propyl ether [56]. Solid lines are calculated with Flory model (Eq. (13)) using coefficients from Table 6.

Table 7

Excess molar volume, V_m^E , temperature derivative of excess molar volume, $(\partial V_m^E / \partial T)_{p,x}$, of (1- and 2-propanol + glyme) liquid mixtures at equimolar composition, at temperature $T = 298.15$ K, and pressure $p = 0.1$ MPa.

Glyme	2-propanol		1-propanol	
	$V_m^E/(\text{cm}^3 \text{mol}^{-1})$	$(\partial V_m^E / \partial T)_{p,x} / 10^{-3}(\text{cm}^3 \text{mol}^{-1} \text{K}^{-1})$	$V_m^E/(\text{cm}^3 \text{mol}^{-1})$	$(\partial V_m^E / \partial T)_{p,x} / 10^{-3}(\text{cm}^3 \text{mol}^{-1} \text{K}^{-1})$
monoglyme	0.176	3.13	−0.071 [58]	1.23 [59]
diglyme	0.105	2.93	−0.068 [58]	2.92 [59]
triglyme	0.023	2.23	−0.120 [60]	2.24 [59]
tetraglyme	−0.044	1.38	−0.202 [59]	1.08 [59]

values for mixtures with *n*-hexane: 0.180 (1-propanol [78]) < 0.410 (2-propanol [84]), which can be explained by the same interactional effect.

Table 8

Excess molar enthalpy, H_m^E , isochoric excess molar internal energy, $U_{m,v}^E$, and OH–O interaction enthalpy, $\Delta H_{\text{OH–O}}$, of (1- and 2-propanol + glyme) liquid mixtures at equimolar composition, at temperature $T = 298.15$ K and pressure $p = 0.1$ MPa.

Glyme	2-propanol			1-propanol		
	$H_m^E/(\text{J mol}^{-1})$	$U_{m,v}^E/(\text{J mol}^{-1})$	$\Delta H_{\text{OH–O}}/(\text{kJ mol}^{-1})$	$H_m^E/(\text{J mol}^{-1})$	$U_{m,v}^E/(\text{J mol}^{-1})$	$\Delta H_{\text{OH–O}}/(\text{kJ mol}^{-1})$
monoglyme	1323	1266	−23.1	1040 [61]	1063	−23.9 [8]
diglyme	1624	1587	−25.4	1214 [62]	1249	−26.6 [8]
triglyme	1846	1837	−28.5	1401 [63]	1450	−30 [8]
tetraglyme	1996	2012	−30.9	1514 [64]	1600	−34.2 [8]

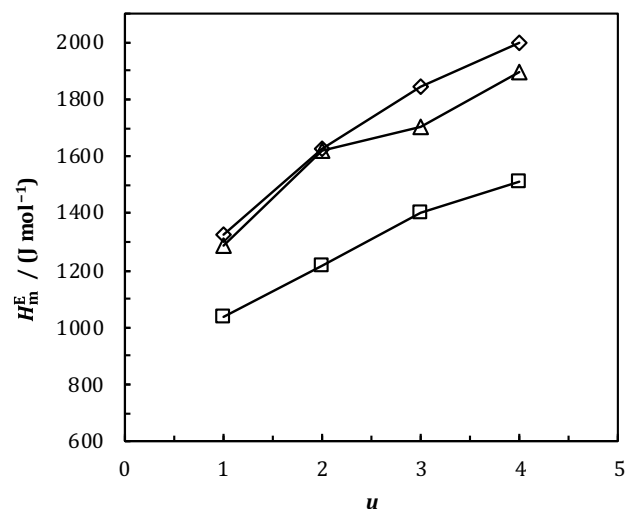


Fig. 5. Excess molar enthalpy, H_m^E , of (glyme + alkane) or (alkanol + glyme) systems as a function of u , the number of oxygen atoms in the glyme, at equimolar composition, $p = 0.1$ MPa and $T = 298.15$ K: (◇) 2-propanol [this work]; (□) 1-propanol [61–64]; (△) *n*-heptane [65].

On the other hand, the high and positive values of the isobaric molar excess heat capacities, $C_{p,m}^E/(\text{J mol}^{-1} \text{K}^{-1})$, for mixtures with *n*-heptane: ≈ 13.5 (1-propanol [85]) and 15.2 (2-propanol [86]), highlight that, in both solutions, the alcohol network is significantly disrupted as the temperature increases. However, the effect is more pronounced

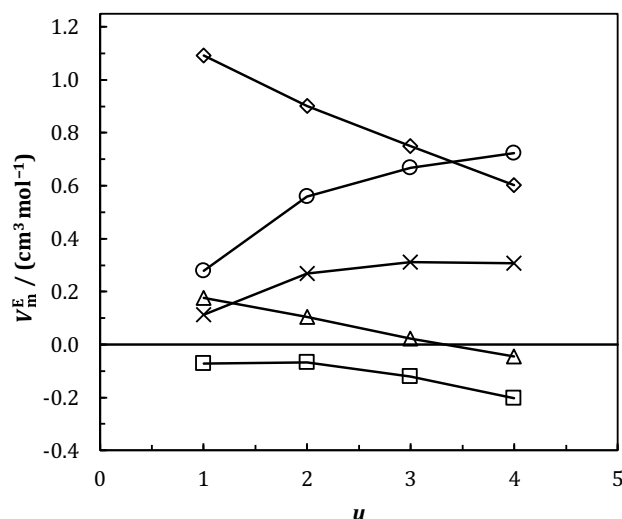


Fig. 6. Excess molar volume, V_m^E , of (glyme + alkane) or (alkanol + glyme) systems as a function of u , the number of oxygen atoms in the glyme, at equimolar composition, $p = 0.1$ MPa and $T = 298.15$ K: (Δ) 2-propanol [this work]; ($\square$) 1-propanol [58–60]; ($\diamond$) n -heptane [34,66,67]; ($\circ$) 1-nonanol [68]; ($\times$) 1-hexanol [69].

when 2-propanol is involved.

5.2. (Glyme + n -alkane) mixtures

Glymes are linear polyethers containing multiple $-O-$ groups within the molecule. They are characterized by both inter and intramolecular dipolar interactions [87]. When glymes are mixed with n -alkanes, these dipolar interactions between glyme molecules are partially disrupted.

For a fixed glyme, H_m^E of (glyme + alkane) mixtures are positive, considerably high and increase with the chain length of the n -alkane. For instance, the $H_m^E / (\text{J mol}^{-1})$ values for (triglyme + n -alkane) are [88]: 1704 (for n -heptane) < 1877 (for n -octane) < 2110 (for n -decane) < 2214 (for n -dodecane). This behavior is a consequence of the intense dipolar interactions between glyme molecules, which are more effectively disrupted by longer alkanes. Interestingly, the (tetraglyme + n -dodecane) mixture exhibits a miscibility gap at 298.15 K in the concentration range $0.20 < x_1 < 0.74$ [89]. The observed immiscibility reflects the inability of n -dodecane to sufficiently disrupt the intense dipolar interactions between molecules of tetraglyme. V_m^E of (glyme + n -alkane) systems for a fixed glyme behaves in a similar way. For example, in (triglyme + n -alkane) solutions, the $V_m^E / (\text{cm}^3 \text{mol}^{-1})$ values are: 0.748 (n -heptane [34]) < 0.970 (n -octane [34]) < 1.272 (n -decane [34]) < 1.478 (n -dodecane [90]).

For a fixed n -alkane (n -heptane), $H_m^E / (\text{J mol}^{-1})$ of (glyme + n -heptane) mixtures increases with the size of the glyme molecule: 1285 (monoglyme [65]) < 1621 (diglyme [91]) < 1704 (triglyme [88]) < 1897 (tetraglyme [92]) (Fig. 5). This can be attributed to the disruption of stronger dipolar interactions by n -heptane in longer glymes, which arise from increasing proximity effects (intramolecular effects) between the oxygen atoms in the glymes [87]. This behavior is also reflected in the values of the partial molar excess enthalpy of glyme at infinite dilution, $\bar{H}_{m,1}^{E,\infty}$, in (glyme + n -heptane) mixtures (see Section 5.4. below). However, structural effects are also relevant in these mixtures, since $V_m^E / (\text{cm}^3 \text{mol}^{-1})$ varies in the opposite direction: 1.092 (monoglyme [67]) > 0.902 (diglyme [66]) > 0.749 (triglyme [34]) > 0.602 (tetraglyme [34]) (Fig. 6). This quantity may even become negative in solutions with components of very different size, such as (tetraglyme + n -pentane), for

which $V_m^E = -0.39 \text{ cm}^3 \text{mol}^{-1}$ [93].

5.3. (Alkanol + glyme) mixtures

In (2-propanol + glyme) mixtures, H_m^E values are large and positive (Table 8, Fig. 5). This can be attributed to a dominant contribution from the breakdown of interactions between molecules of the same chemical species. Notably, for systems with a given glyme, H_m^E follows the sequence: (2-propanol + glyme) > (glyme + n -heptane) > (2-propanol + n -heptane) (see Fig. 5). This clearly indicates that self-association and solvation effects are of minor importance in (2-propanol + glyme) mixtures, which are largely unstructured. For the (2-propanol + di- n -propyl ether, DPE) system, $H_m^E / (\text{J mol}^{-1}) = 958$ [94], a value close to that of the (2-propanol + n -heptane) system (797 J mol^{-1} [83]). This suggests that alcohol self-association effects remain relevant in the latter mixture.

For longer glymes, H_m^E is higher, and the maxima of the corresponding $H_m^E(x_1)$ curves are shifted toward higher concentrations of 2-propanol (Fig. 2). This can be interpreted as a consequence of the increased ability of longer polyether chains to break (2-propanol)-(2-propanol) interactions. The corresponding values of the isochoric excess molar internal energy, $U_{m,V}^E$ (Table 8), which increase more rapidly than the H_m^E values with the glyme size, support this interpretation. It should be noted that the equation of state term is rather small for these systems, so the H_m^E values are mainly determined by interactional effects. Note that, for the (2-propanol + DPE) system, the $H_m^E(x_1)$ curve is skewed to lower mole fractions of the alkanol (Fig. 4), further suggesting that self-association effects are still significant in this mixture.

In contrast with these H_m^E values, the V_m^E values for (2-propanol + glyme) solutions are either small and positive (monoglyme, diglyme and triglyme) or negative (tetraglyme) (see below). Systems exhibiting such values of V_m^E , along with largely positive H_m^E results, are characterized by strong structural effects that outweigh the positive interactional contribution to V_m^E arising from the rupture of interactions between like molecules. The relative influence of structural effects on $V_m^E / (\text{cm}^3 \text{mol}^{-1})$ appears to increase with glyme size, as this excess function becomes progressively lower: 0.176 (monoglyme) > 0.105 (diglyme) > 0.023 (triglyme) > -0.044 (tetraglyme) (Table 7 and Fig. 6). Note that these variations are the same as those for (glyme + n -heptane) mixtures (see Section 5.2 above). The values of $(\partial V_m^E / \partial T)_{p,x}$ (Table 7) are positive, indicating that the interactional contribution to V_m^E increases with temperature. However, $(\partial V_m^E / \partial T)_{p,x}$ decreases as glyme size increases (Table 7), which may be due to the growing relevance of structural effects under these conditions.

(1-Propanol + glyme) mixtures are characterized by analogous properties to those of (2-propanol + glyme) solutions. However, for a fixed glyme, replacing 2-propanol with 1-propanol leads to lower values of both H_m^E and V_m^E (Tables 7, 8, and Figs. 5, 6). This behavior can be explained, at least partially, by the combination of the following factors: (i) Glyme molecules break the hydrogen bonding network of 2-propanol more effectively than that of the 1-propanol. This phenomenon is also observed in (alkanol + n -heptane) mixtures (see Section 5.1 above). (ii) Alkanol-glyme interactions are likely stronger in the case of 1-propanol, as its $-OH$ group is less sterically hindered, resulting in a more negative contribution to the excess functions. (iii) For the same reason, the number of unlike molecules interactions formed upon mixing is greater in these solutions. It is worth noting that in systems such as (1-propanol or 2-propanol + glyme) and (glyme + n -heptane), both excess functions, H_m^E and V_m^E , vary similarly with glyme size (Figs. 5 and 6). This highlights the relevance of both physical interactions and structural effects in the mixtures of alkanols studied. The larger values of $(\partial V_m^E / \partial T)_{p,x}$ observed for (1-propanol + glyme) systems (Table 7) may be explained

by the fact that glymes more effectively disrupt the self-association of 2-propanol.

5.4. Analysis of different contributions to excess molar enthalpy

Next, the enthalpy of interaction between 2-propanol and glymes, denoted as $\Delta H_{\text{OH-O}}$, is evaluated using the equation [8,95]:

$$\begin{aligned} \Delta H_{\text{OH-O}} = & \bar{H}_{m,1}^{\text{E},\infty} (2\text{-propanol} + \text{glyme}) \\ & - \bar{H}_{m,1}^{\text{E},\infty} (2\text{-propanol} + n\text{-heptane}) \\ & - \bar{H}_{m,1}^{\text{E},\infty} (\text{glyme} + n\text{-heptane}) \end{aligned} \quad (16)$$

where $\bar{H}_{m,1}^{\text{E},\infty}$ represents the partial excess molar enthalpy of the first component of the mixture at infinite dilution. In the calculation of $\Delta H_{\text{OH-O}}$, several considerations have been taken into account:

(i) The values of $\bar{H}_{m,1}^{\text{E},\infty}$ for (2-propanol + glyme) mixtures are obtained from our measurements of H_m^{E} over the entire mole fraction range. The Redlich-Kister fit is used to calculate these values from the following expression:

$$\bar{H}_{m,1}^{\text{E},\infty} = \lim_{x_1 \rightarrow 0} \left[H_m^{\text{E}} + x_2 \left(\frac{\partial H_m^{\text{E}}}{\partial x_1} \right)_{T,P} \right] = \sum_{i=0}^{k-1} (-1)^i A_i \quad (17)$$

where the parameters A_i are listed in Table 5. Accordingly, the values of $\bar{H}_{m,1}^{\text{E},\infty} / (\text{kJ mol}^{-1})$ are: 5.6 (monoglyme); 5.9 (diglyme); 5.5 (triglyme); 5.6 (tetraglyme).

(ii) As is customary in the application of association theories, it is assumed that $\bar{H}_{m,1}^{\text{E},\infty} (2\text{-propanol} + n\text{-heptane})$ is independent of the alcohol [63,79–82]. In this work, we have used $\bar{H}_{m,1}^{\text{E},\infty} (2\text{-propanol} + n\text{-heptane}) = 23.2 \text{ kJ mol}^{-1}$, which is the same value reported for mixtures with 1-alkanols [96–98].

(iii) Finally, the values of $\bar{H}_{m,1}^{\text{E},\infty} / (\text{kJ mol}^{-1})$ for (glyme + n -heptane) mixtures are: 5.5 (monoglyme) [65]; 8.2 (diglyme) [91]; 10.8 (triglyme) [88]; 13.3 (tetraglyme) [92]. These values are consistent with the statement made above regarding the stronger dipolar interactions exhibited by longer glymes (see Section 5.2).

An inspection of the $\Delta H_{\text{OH-O}}$ results, collected in Table 8, reveals several interesting findings: (i) Increasing the glyme size in mixtures with a fixed alkanol (1-propanol or 2-propanol) leads to more negative $\Delta H_{\text{OH-O}}$ values, indicating stronger interactions between unlike molecules. This is in accordance with the stronger polar character of longer glymes, as reflected in the $\bar{H}_{m,1}^{\text{E},\infty} (\text{glyme} + n\text{-heptane})$ values. (ii) Although the $\Delta H_{\text{OH-O}}$ values are similar for both alkanols, 1-propanol consistently shows a higher contribution to interactions between unlike molecules, especially in mixtures with tetraglyme. This can be attributed, as previously discussed, to the fact that the –OH group in 2-propanol is more sterically hindered, reducing its ability to participate in interactions between unlike molecules. (iii) The large and negative $\Delta H_{\text{OH-O}}$ values contrast with the large and positive H_m^{E} results, indicating that the latter are predominantly determined by the breaking of interactions between like molecules.

We have also determined the $\Delta H_{\text{OH-O}}$ values for the (1-propanol or 2-propanol + DPE) systems. For this purpose, we used the following values of $\bar{H}_{m,1}^{\text{E},\infty} / (\text{kJ mol}^{-1})$: 0.8 (DPE + n -heptane) [99]; 6.6 (1-propanol + DPE); 7.5 (2-propanol + DPE) [56]. Thus, the resulting $\Delta H_{\text{OH-O}} / (\text{kJ mol}^{-1})$ values are: –15.8 (1-propanol + DPE); –14.9 (2-propanol

+ DPE). These values are less negative than those obtained for the corresponding solutions with glymes, indicating that interactions between unlike molecules are stronger in the latter mixtures. This is likely because the number of oxygen atoms is higher in polyethers and the –O– group is very sterically hindered in DPE. The lower values of $H_m^{\text{E}} / (\text{J mol}^{-1})$ for the systems with DPE (740 (1-propanol); 958 (2-propanol)) [56] suggest that this ether is not an effective breaker of alcohol self-association, which plays a crucial role in determining the thermodynamic properties of these solutions.

5.5. Results from the Flory model

Firstly, the low values of $\sigma_r(H_m^{\text{E}})$ for mixtures with linear polyethers are noteworthy (Table 6). This indicates that the random mixing hypothesis is largely valid for these systems, which exhibit weak orientational effects. In other words, physical interactions dominate. In contrast, the $\sigma_r(H_m^{\text{E}})$ result obtained for the (2-propanol + DPE) system is significantly higher, clearly indicating the importance of orientational effects in this solution. Notably, the H_m^{E} curve of this system is skewed toward low mole fractions of the alkanol (Fig. 4), a typical feature of solutions in which alcohol self-association plays a determining role.

It should also be noted that there is a significant difference between the values of the interactional parameter, X_{12} , for systems containing polyethers compared to the corresponding value for the solution with DPE (Table 6). This highlights that interactions between like molecules are much more prominent in the former mixtures.

The excess molar volumes are poorly represented by the model, with theoretical results significantly exceeding the experimental values. This indicates that the model overestimates the interactional contribution to the excess volume. Nevertheless, the theory correctly describes the trend observed in mixtures with polyethers: the decrease in V_m^{E} as the number of O atoms in the ether increases.

Finally, it should be emphasized that the model provides similar results for (1-propanol or 2-propanol + glyme) mixtures. Accordingly, the mean relative standard deviations calculated from the formula:

$$\bar{\sigma}_r(H_m^{\text{E}}) = \frac{1}{N_s} \sum \sigma_r(H_m^{\text{E}}) \quad (18)$$

are 0.040 (1-propanol) [8]; 0.044 (2-propanol) (with $N_s = 4$, the number of systems considered). Consequently, orientational effects are also weak in systems containing 1-propanol.

6. Conclusions

Densities at atmospheric pressure and temperatures $T = (293.15 \text{ to } 303.15) \text{ K}$ have been measured for the systems [2-propanol + $(\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_u\text{CH}_3)$ with $u = 1, 2, 3, 4$. Excess molar enthalpies at $T = 298.15 \text{ K}$ and the same pressure are also reported. The values of H_m^{E} are large and positive, indicating that the disruption of interactions between molecules of the same species is the dominant contribution to this excess function. In contrast, the corresponding V_m^{E} values are small or even negative (in the case of the solution with tetraglyme), suggesting that V_m^{E} is primarily determined by structural effects. Analysis of the results using the Flory model reveals that orientational effects are weak in the studied systems and significantly stronger in the (2-propanol + di- n -propyl ether) mixture. Mixtures of 1-propanol or 2-propanol and glymes exhibit similar behavior, although interactions between unlike molecules are stronger in the solutions containing 1-propanol.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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Data availability

Data will be made available on request.

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