Temperature dependence of excess properties in alcohols + ethers mixtures.
I. Excess molar volumes of 1-propanol or 1-hexanol + ethers at 318.15 K

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Abstract

Excess molar volumes V_m^E at 318.15 K and atmospheric pressure for 1-propanol or 1-hexanol + dibutyl ether, 1-propanol or 1-hexanol + 2,5-dioxahexane, 1-propanol or 1-hexanol + 2,5,8-trioxanonane, 1-propanol or 1-hexanol + 3,6,9-trioxaunde-cane and 1-propanol or 1-hexanol + 5,8,11-trioxapentadecane, have been obtained from densities measured with an Anton-Paar DMA 602 vibrating-tube densimeter. All the excess volumes are negative over the whole mole fraction range, except for the systems 1-propanol + 2,5,8-trioxanonane, which is S-shaped, and for 1-hexanol + 2,5-dioxahexane or 1-hexanol + 2,5,8-trioxanonane which are positive over the whole mole fraction range. For the systems with 1-propanol the V_m^E curves are shifted to the region rich in the alkanol, increasing their asymmetry with the number of oxygen groups in the ether. For 1-hexanol systems the V_m^E curves are symmetrical. This behaviour can be attributed to free volume effects.

The sign of dV_m^E/dT is discussed. Systems with 1-propanol are characterized by $dV_m^E/dT > 0$, which may be due to the more self-associated character of the alcohol. In solutions with 1-hexanol, the sign of dV_m^E/dT depends on the ether considered, i.e. on the balance between the interactional and structural contributions. So, if the latter are more important, then $dV_m^E/dT > 0$.

Results remark the differences between systems containing *n*-alkanols and monoethers or polyethers. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Mixtures containing oxygenated compounds, such as ethers (–O– group) and alkanols (–OH– group), are of great importance from a practical point of view as they are increasingly used as additives to gasoline owing to their octane-enhancing and pollution-redu-cing properties.

From a theoretical point of view, solutions invol-ving oxaalkanes are of high interest because they make it possible to study a number of effects (e.g. steric or proximity effects, cyclization) on the inter-actions present in the mixture considered. Binary

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systems of oxaalkanes and 1-alkanols are particularly interesting due to their complexity, consequence of the self-association of the alkanols partially destroyed by the active molecules of ethers, and of the new *intermolecular* OH–O bonds created. So, the treatment of this class of mixtures is a severe test for any theoretical model. Moreover, the analysis of the present systems is a previous step to study mixtures containing hydroxyethers, where the intramolecular effects between the –OH and –O– groups of cellosolves become of great importance [1–8].

DISQUAC [9,10], a purely physical model, has been successfully applied to the mixtures under study by considering structure-dependent interaction parameters [11]. In this way, properties as excess molar enthalpies, H_m^E, or excess molar heat capacities at constant pressure, $C_{p,m}^E$, which are very sensitive to molecular structure are properly represented by DISQUAC. The Dortmund version of UNIFAC [12], which ignores proximity or steric effects fails to describe the mentioned properties [11]. Unfortunately, both the DISQUAC and the UNIFAC models are based on rigid lattice theories and hence $V_m^E = 0$, a useful property to evaluate, e.g. changes in free volume or interstitial accommodation. The model more widely applied to represent simultaneously H_m^E and V_m^E is the so-called ERAS model [13], which combines the chemical, physical and equation of state contributions, the two later being expressed by the Flory equation of state [14]. However, as far as we know, the ERAS model has been merely applied to mixtures of 1-propanol with 2,5,8-trioxanonane, or with 2,5,8,11-tetraoxadodecane [15]. The lack of a systematic treatment of the present mixtures in the framework of the ERAS model underlines the difficulty in studying such mixtures.

As a continuation of our previous experimental studies on binary mixtures containing oxaalkanes and/or 1-alkanols [16–28], and in order to extend the available database for alkanols + ethers mixtures, we present the first work of a series in which the temperature dependence of excess properties will be analysed. Particularly, we report here V_m^E of systems formed by 1-propanol or 1-hexanol with dibutyl ether, 2,5-dioxahexane, 2,5,8-trioxanonane, 3,6,9-trioxaundecane, 5,8,11-trioxapentadecane, over the whole mole fraction range at atmospheric pressure and at 318.15 K.

2. Experimental

2.1. Materials

All the chemicals used were from Fluka: 1-propanol, dibutyl ether, 2,5-dioxahexane and 2,5,8-trioxanonane (puriss p.a., >99.5%); 1-hexanol and 3,6,9-trioxaundecane (puriss, >99%), and 5,8,11-trioxapentadecane (purum, >98%), were used as received. Prior to the measurements, the chemicals were carefully dried with molecular sieve (Union Carbide type 4Å beads, from Fluka), added to liquids. The results of the measurements of their densities at 298.15 and 318.15 K and atmospheric pressure are listed in Table 1. They are in good agreement with published values.

2.2. Apparatus and procedure

An Anton-Paar DMA 602 vibrating-tube densimeter [29–31], operating under static conditions, was used to determine the densities, ρ, of the pure liquids and of their binary mixtures. The oscillation period τ (of about 3.6 ms) 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 measurements, and for each pure liquid or mixture three runs were developed. Protection against the generation of static electricity around the instrument and temperature stability were effective in maintaining an overall stable indication of $\Delta\tau = \pm 5$ ns, and hence $|\Delta\tau/\tau| = 1.4 \times 10^{-6}$. This gives a resolution in density of $|\Delta\varrho/\varrho| = 6 \times 10^{-6}$, where the errors due to calibration and the density of the references liquid are not taken into account. All the measuring operation and calculations were computer controlled.

Before each series of measurements the instrument was calibrated with doubly distilled and degassed water and 'vacuum'. The accuracy in the determination of ρ is believed to be less than $\pm 2 \times 10^{-2}$ kg/m^3. Hexane and acetone or ethanol were used for rinsing the cell tube between measurements. More details are given elsewhere [32]. Temperature was evaluated by a quartz thermometer. The densimeter was thermostated to ± 0.004 K and measurements were carried out at 318.15 K and atmospheric pressure.

Table 1
Experimental densities, ρ, of the pure compounds at 298.15 and 318.15 K and atmospheric pressure

Compound	ρ (g/cm^3)			
	298.15 K		318.15 K	
	This work	Literature	This work	Literature
1-Propanol	0.79955	0.7996[a]	0.78329	0.7830[e]
				0.78359[f]
1-Hexanol	0.81517	0.81534[a]	0.80079	0.80126[g]
Dibutyl ether	0.76383	0.7641[a]	0.74639	–
2,5-Dioxahexane	0.86122	0.86132[b]	0.83912	0.84362[g]
2,5,8-Trioxanonane	0.93879	0.93870[c]	0.91886	–
3,6,9-Trioxaundecane	0.9039	0.9039[d]	0.88263	–
5,8,11-Trioxapentadecane	0.87935	0.87862[d]	0.86176	–

[a]Riddick et al. [49].
[b]Muhuri and Hazra [50].
[c]Kimura et al. [51].
[d]Carmona et al. [26].
[e]Ortega [52].
[f]Díaz Peña and Tardajos [53].
[g]Riddick et al. [49] extrapolated at 318.15 K.

Binary mixtures were prepared by mass in small vessels of about 10 cm^3. Caution was taken to prevent evaporation, and the error in the final mole fraction is estimated to be less than ±0.0001. Conversion to molar quantities was based on the relative atomic mass table of 1985 issued by IUPAC. [33].

The excess molar volumes were calculated from the densities of the pure liquids and their mixtures. As in order to obtain reliable results for V_m^E the absolute value of ρ are less important compared to the relative certainty in ρ [32], the accuracy in V_m^E is believed to be less than ±$(0.01|V_{m,M}^E| + 0.005 \text{ cm}^3/\text{mol})$, where $V_{m,M}^E$ denotes the maximum absolute experimental value of the excess molar volume with respect to x (mole fraction of 1-alcohol).

3. Results

The results of V_m^E as a function of mole fraction of the alkanol, x, are collected in Table 2. The data were fitted by unweighted least-squares polynomial regression to the equation:

$$V_m^E = x(1-x)\sum_{i=0}^{k} A_i(2x-1)^i \tag{1}$$

The number of coefficients k used in Eq. (1) for each mixture was determined by applying an F-test [34] at the 95% confidence level. Table 3 lists the parameters A_i obtained in the regression, together with the standard deviations σ; defined by:

$$\sigma(V_m^E) = \left[\frac{\sum(V_{m,cal.}^E - V_{m,exp.}^E)}{(N-k)}\right]^{1/2} \tag{2}$$

where N stands for the number of direct experimental values. For all the mixtures $\sigma(V_m^E)/|V_{m,M}^E| < 0.017$, in accord with the precision attainable with the instrument used. A graphical representation of the experimental results together with the smoothing curves are shown in Figs. 1 and 2. No data have been found in literature for comparison.

4. Discussion

Firstly, we present a summary of some main features of 1-alkanols or linear oxaalkanes + n-alkanes systems.

4.1. Alkanols + n-alkanes mixtures

It is well known that here V_m^E is the result of several opposing effects [35,36]: changes in self-association

Table 2
Excess molar volumes for the mixtures 1-propanol (x) or 1-hexanol (x) + ethers($1 - x$) at 318.15 K and atmospheric pressure

x	V_m^E (cm³/mol)	x	V_m^E (cm³/mol)	x	V_m^E (cm³/mol)
1-Propanol + dibutyl ether					
0.0954	−0.0266	0.4429	−0.1185	0.7532	−0.1281
0.1413	−0.0403	0.5019	−0.1276	0.7741	−0.1226
0.1970	−0.0560	0.5378	−0.1318	0.8492	−0.0991
0.2355	−0.0687	0.6066	−0.1380	0.9003	−0.0763
0.2880	−0.0843	0.6479	−0.1372	0.9496	−0.0431
0.3679	−0.1032	0.7045	−0.1341		
1-Propanol + 2,5-dioxahexane					
0.0449	−0.0019	0.4058	−0.0402	0.7000	−0.0471
0.0933	−0.0061	0.4556	−0.0429	0.7516	−0.0435
0.1473	−0.0121	0.5016	−0.0468	0.7914	−0.0395
0.1951	−0.0167	0.5696	−0.0485	0.8531	−0.0318
0.2497	−0.0235	0.6008	−0.0491	0.9012	−0.0226
0.3037	−0.0301	0.6535	−0.0486	0.9514	−0.0124
0.3542	−0.0360				
1-Propanol + 2,5,8-trioxanonane					
0.0551	0.0034	0.4007	−0.0172	0.7024	−0.0363
0.1013	0.0033	0.4513	−0.0213	0.7503	−0.0348
0.1502	0.0005	0.5001	−0.0260	0.7973	−0.0331
0.1976	−0.0003	0.5460	−0.0290	0.8442	−0.0302
0.2490	−0.0040	0.6030	−0.0332	0.8981	−0.0245
0.2975	−0.0078	0.6533	−0.0354	0.9469	−0.0137
0.3457	−0.0115				
1-Propanol + 3,6,9-trioxaundecane					
0.0587	−0.0451	0.3567	−0.2269	0.6559	−0.2820
0.1035	−0.0758	0.3972	−0.2434	0.7510	−0.2593
0.1560	−0.1126	0.4545	−0.2624	0.8070	−0.2282
0.2049	−0.1441	0.5085	−0.2753	0.8526	−0.1951
0.2554	−0.1739	0.5476	−0.2817	0.8995	−0.1503
0.3074	−0.2011	0.6027	−0.2851	0.9500	−0.0859
1-Propanol + 5,8,11-trioxapentadecane					
0.0604	−0.0418	0.3943	−0.2556	0.6946	−0.3024
0.1109	−0.0794	0.4485	−0.2776	0.7526	−0.2869
0.1491	−0.1076	0.4979	−0.2943	0.7954	−0.2682
0.2067	−0.1478	0.5551	−0.3038	0.8510	−0.2248
0.2556	−0.1814	0.6039	−0.3082	0.8990	−0.1732
0.3003	−0.2097	0.6546	−0.3094	0.9481	−0.1026
0.3461	−0.2342				
1-Hexanol + dibutyl ether					
0.0546	−0.0768	0.4004	−0.3358	0.7005	−0.3052
0.1025	−0.1408	0.4516	−0.3471	0.7485	−0.2759
0.1487	−0.1878	0.5014	−0.3537	0.8010	−0.2391
0.1993	−0.2324	0.5505	−0.3473	0.8529	−0.1918
0.3034	−0.3006	0.5996	−0.3401	0.8995	−0.1410
0.3461	−0.3219	0.6525	−0.3255	0.9471	−0.0780
1-Hexanol + 2,5-dioxahexane					
0.0503	0.0267	0.3469	0.0924	0.7012	0.0680
0.0970	0.0460	0.4519	0.0942	0.7412	0.0610
0.1510	0.0625	0.5051	0.0913	0.8033	0.0477
0.2052	0.0746	0.5510	0.0863	0.8501	0.0359

Table 2 (*Continued*)

x	V_m^E (cm³/mol)	x	V_m^E (cm³/mol)	x	V_m^E (cm³/mol)
0.2491	0.0808	0.5948	0.0819	0.8985	0.0238
0.2982	0.0882	0.6585	0.0746	0.9501	0.0101
1-Hexanol + 2,5,8-trioxanonane					
0.0537	0.0660	0.3987	0.2921	0.6992	0.2508
0.1003	0.1159	0.4452	0.3010	0.7495	0.2242
0.1560	0.1667	0.5017	0.3033	0.7974	0.1916
0.2071	0.2074	0.5503	0.2991	0.8525	0.1488
0.2532	0.2371	0.6027	0.2864	0.9001	0.1051
0.3051	0.2641	0.6500	0.2731	0.9471	0.0565
0.3537	0.2798				
1-Hexanol + 3,6,9-trioxaundecane					
0.0596	−0.0061	0.4050	−0.0528	0.7000	−0.0630
0.1047	−0.0116	0.4528	−0.0578	0.7496	−0.0595
0.2012	−0.0259	0.4977	−0.0609	0.8016	−0.0556
0.2498	−0.0333	0.5528	−0.0638	0.8512	−0.0503
0.3013	−0.0412	0.6019	−0.0648	0.9009	−0.0402
0.3666	−0.0487	0.6493	−0.0640	0.9483	−0.0257
1-Hexanol + 5,8,11-trioxapentadecane					
0.0585	−0.0357	0.4028	−0.1960	0.7033	−0.1967
0.1012	−0.0615	0.4520	−0.2071	0.7495	−0.1865
0.1526	−0.0875	0.4972	−0.2130	0.7986	−0.1623
0.2008	−0.1156	0.5539	−0.2144	0.8503	−0.1342
0.2615	−0.1449	0.6036	−0.2143	0.8939	−0.1069
0.2965	−0.1594	0.6475	−0.2094	0.9409	−0.0666
0.3589	−0.1833				

and physical interactions (dipole–dipole) between alkanol multimers and monomers lead to an increasing of volume; a decreasing of volume is obtained by changes of free volume and interstitial accommodation [35,36]. The magnitudes of these contributions are sensitive to the lengths of component molecules [35,36]. So, as the length of the 1-alkanol is increased, the negative effect accompanying the fitting of the n-alkanes molecules into the alkanol multimer structure becomes progressively more important, and predominates for sufficient long alkanol molecules, e.g. for n-heptane, V_m^E is positive over the whole range of concentration for lower alkanols and becomes sigmoid for longer alkanols.

Table 3
Coefficients A_i and standard deviations $\sigma(V_m^E)$ for representation of the excess molar volumes at 318.15 K and atmospheric pressure by Eq. (1)

| System	A_0	A_1	A_2	A_3	A_4	$\sigma(V_m^E)$ (cm³/mol)
1-Propanol + dibutyl ether	−0.5108	−0.271	−0.098	−0.096	–	0.0007
+2,5-Dioxahexane	−0.1860	−0.099	0.028	−0.026	–	0.0004
+2,5,8-Trioxanonane	−0.1027	−0.161	−0.013	−0.031	–	0.0006
+3,6,9-Trioxaundecane	−1.0959	−0.425	−0.165	−0.156	−0.10	0.0006
+5,8,11-Trioxapentadecane	−1.1721	−0.509	−0.283	−0.311	–	0.0010
1-Hexanol + dibutylether	−1.4051	−0.031	−0.200	–	–	0.0015
+2,5-Dioxahexane	0.3648	−0.106	0.041	−0.084	–	0.0009
+2,5,8-Trioxanonane	1.2117	−0.051	0.030	−0.037	–	0.0010
+3,6,9-Trioxaundecane	−0.2436	−0.109	–	−0.145	−0.103	0.0006
+5,8,11-Trioxapentadecane	−0.850	−0.198	−0.058	−0.14	–	0.0014
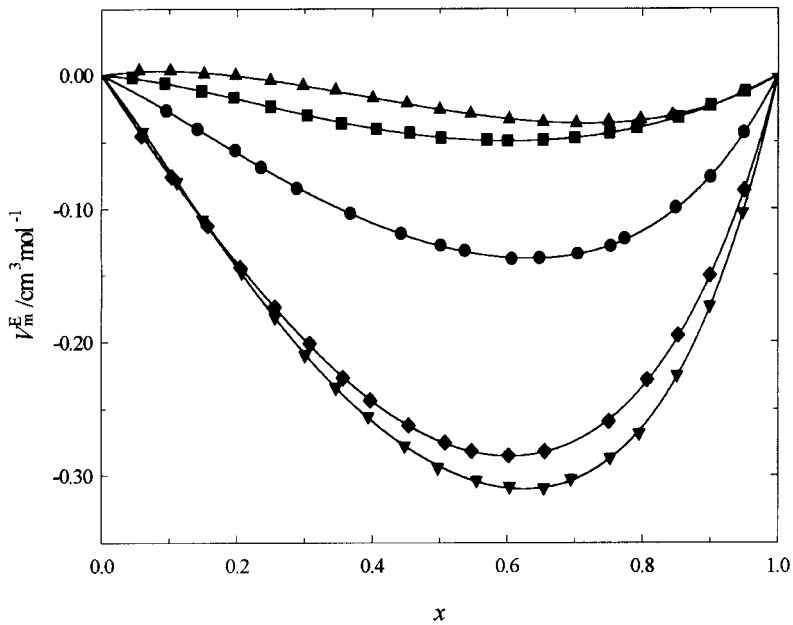
Fig. 1. Excess molar volumes V_m^E at 318.15 K for 1-propanol + ethers mixtures versus x, the mole fraction of 1-propanol: (●) dibutyl ether; (■) 2,5-dioxahexane; (▲) 2,5,8-trioxanonane; (◆) 3,6,9-trioxaundecane; (▼) 5,8,11-trioxapentadecane. Full curves represent the smoothing Eq. (1) with the coefficients of Table 3.
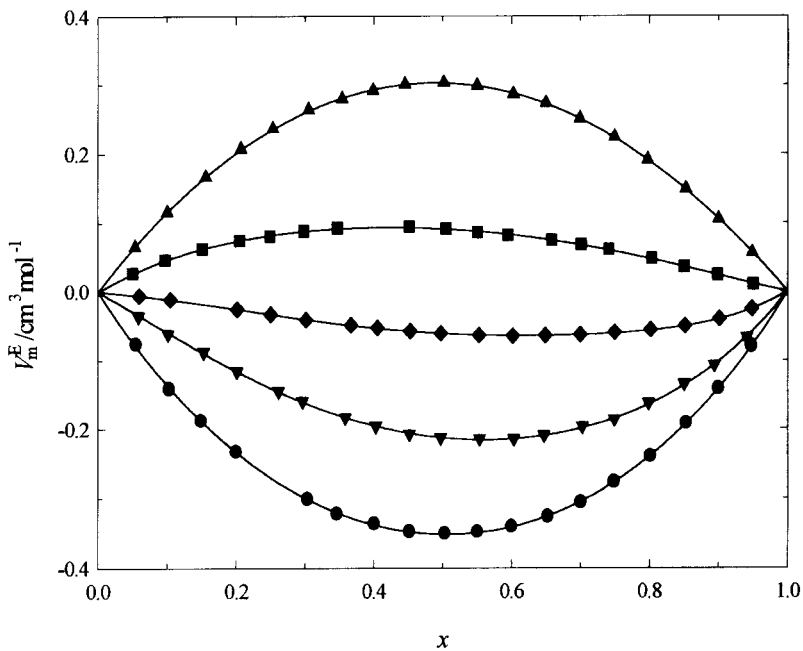

Fig. 2. Excess molar volumes V_m^E at 318.15 K for 1-hexanol + ethers mixtures versus x, the mole fraction of 1-hexanol: (●) dibutyl ether; (■) 2,5-dioxahexane; (▲) 2,5,8-trioxanonane; (◆) 3,6,9-trioxaundecane; (▼) 5,8,11-trioxapentadecane. Full curves represent the smoothing Eq. (1) with the coefficients of Table 3.

Regarding dV_m^E/dT in 1-alkanol + n-alkane mixtures, this quantity is positive for systems with positive V_m^E, and is negative for systems or concentration ranges where V_m^E is negative [18,19,37–39]. This behaviour has been attributed to a variation in the balance of the associational and non-specific interactions and the free volume effects with temperature, depending on the size and shape of the components molecules [39]. For systems with a short alkanol and long alkane, V_m^E and dV_m^E/dT are positive over the whole concentration range due to the predomination of the effect of disruption of the H-bonds and no-specific interactions over the less significant free volume contribution. In contrast, systems with a long alkanol and short alkane molecules, V_m^E and dV_m^E/dT are negative, which is attributed to the increasing predomination of the negative free volume contribution with rising temperature over the positive contributions [39].

4.2. Linear oxaalkanes + n-alkanes mixtures

In this type of solutions, the dipole–dipole interactions between ether molecules are weakened by the addition of the alkane. The sign of V_m^E and dV_m^E/dT depends on the relative size of the mixtures compounds [40,41]. For di-n-propylether + n-heptane, where the molecular size of both components are similar and free volume effects are small, V_m^E and dV_m^E/dT are both positive over the whole range of concentration [40]. In exchange, for systems comprising longer ether and shorter alkane molecules, e.g. di-n-dibutylether + n-hexane, free volume contributions are relatively more important and V_m^E and dV_m^E/dT are both negative [41].

The V_m^E of linear polyethers + n-alkanes are usually higher than those of linear ethers + n-alkanes, indicating larger differences between positive and negative contributions [42]. It is remarkable that in systems of $CH_3-O-(CH_2-CH_2-O)_m-CH_3$ (glymes) with n-pentane, V_m^E becomes S-shaped for $m = 3, 4$ [43]. Moreover, dV_m^E/dT is usually positive and becomes negative for $CH_3-O-(CH_2-CH_2-O)_4-CH_3 + n$-$C_7$. This behaviour is still under discussion. Lately, it has been attributed to the presence of order in pure glymes, probably constructed as weak H-bonding [44].

4.3. Alkanols + oxxalkanes mixtures

Now, one must also taken into account interactions between unlike molecules, i.e. the new OH–O bonds created, which contribute negatively to V_m^E.

We note that for a given polyether, V_m^E ($x = 0.5$) increases with the size of the alcohol, which is independent of the system temperature [26,27]. Such variation has been attributed to [26,27]: (a) interaction effects, as the H_m^E also increases, i.e. the number of broken H-bonds is larger for longer alcohols and is not balanced by the OH–O created; the destruction of the oxygen–oxygen interactions by the alkyl chain of the alkanol, which increases with its length, also contributes positively to V_m^E; (b) free volume effects which are more important in mixtures containing short alkanol molecules. When the chain length of both components is increased, the contribution from interstitial accommodation might be sufficiently negative for V_m^E to become negative as in the case of the 1-nonanol + 5,8,11-trioxapentadecane [27].

We also note that for solutions of a given alcohol with oxaalkanes which differ only in their n-alkyl end length chain, V_m^E ($x = 0.5$) decreases with the size of the ether. This may be due to ethers with larger chain ends are less active to break the self-association of the alkanols as the –O– groups are more hindered [26,27].

V_m^E curves are shifted to high x values for mixtures with 1-propanol and are symmetrical for systems including 1-hexanol, which may be attributed to free volume effects [26].

Our results remark that solutions of 1-alkanols and linear monoethers behave quite differently [21]. For each monoether, V_m^E increases from methanol to 1-propanol and then decreases. H_m^E varies as 1-alkanol + n-alkane mixtures when the alkane is fixed: increases from methanol to 1-propanol and then decreases slowly [20]. It suggests that for longer alkanols, the interactional contribution is practically the same, while the structural effects increases. Such different behaviour may be attributed to H_m^E is higher for solutions with polyethers that for mixtures with monoethers, i.e. to a more important interactional contribution to V_m^E, in part related to the strong dipole–dipole interactions between polyethers molecules more easily broken by longer 1-alkanols. It is remarkable that other mixtures including 1-alkanols show similar behaviour: 1-alkanols + 2-butanone

Table 4
V_m^E ($x = 0.5$) at 318.15 and 298.15 K and atmospheric pressure for 1-propanol or 1-hexanol + oxaalkane mixtures

System	V_m^E ($x = 0.5$)	
	318.15 K	298.15 K
1-Propanol + dibutylether	−0.1278	−0.1846[a]
1-Propanol + 2,5-dioxahexane	−0.0465	−0.0677[b]
1-Propanol + 2,5,8-trioxanonane	−0.0257	−0.0681[b]
1-Propanol + 3,6,9-trioxaundecane	−0.2740	−0.3044[b]
1-Propanol + 5,8,11-trioxapentadecane	−0.2930	−0.3523[b]
1-Hexanol + dibutylether	−0.3513	−0.3415[a]
1-Hexanol + 2,5-dioxahexane	+0.0912	+0.1127[c]
1-Hexanol + 2,5,8-trioxanonane	+0.3029	+0.2685[c]
1-Hexanol + 3,6,9-trioxaundecane	−0.0609	−0.0283[c]
1-Hexanol + 5,8,11-trioxapentadecane	−0.2125	−0.2332[c]

[a] Serna et al. [20].
[b] Serna et al. [21].
[c] Serna et al. [28].

[45]; methyl alkanoates [46], +ethyl acetate [47], +2-ethoxyethanol [48].

For 1-propanol mixtures, we note that dV_m^E/dT is positive (Table 4). In the case of systems with 1-hexanol, $dV_m^E/dT < 0$ for di-n-butylether and 3,6,9-trioxaundecane and $dV_m^E/dT > 0$ for 2,5-dioxahexane, 2,5,8-trioxanonane and 5,8,11-trioxapentadecane (Table 4). In view of the general features described above for 1-alkanol or oxaalkane + n-alkane mixtures, the observed behaviour may be attributed, in the case of 1-propanol systems, to the more self-associated character of this alcohol (larger number of broken H-bonds with increasing temperature). It seems that the negative contribution to V_m^E from free volume effects increases with temperature and predominates in the case of systems with 1-hexanol. However, it might occur that the interactional contribution (large H_m^E) become sufficiently important in such way that the sign of dV_m^E/dT is inverted.

5. Conclusions

V_m^E at 318.15 K and atmospheric pressure are reported for 1-propanol or 1-hexanol + dibutyl ether, 1-propanol or 1-hexanol + 2,5-dioxahexane, 1-propanol or 1-hexanol + 2,5,8-trioxanonane, 1-propanol or 1-hexanol + 3,6,9-trioxaundecane and 1-propanol or 1-hexanol + 5,8,11-trioxapentadecane systems.

Mixtures with 1-propanol are characterized by $dV_m^E/dT < 0$ which may be attributed to the more self-associated character of the alcohol. In solutions with 1-hexanol, the sign of dV_m^E/dT depends on the ether considered, i.e. on the balance between the interactional and structural contributions; when the latter are predominant, then $dV_m^E/dT < 0$.

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