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Thermodynamic properties of *n*-alkoxyethanols + organic solvent mixtures
XVIII. Excess volumes at 298.15 K for 2-(2-alkoxyethoxy)ethanol + *n*-polyether

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Abstract

Excess molar volumes, V^E at 298.15 K and atmospheric pressure for 2-(2-methoxyethoxy)ethanol or 2-(2-butoxyethoxy)ethanol+2,5-dioxahexane, +2,5,8-trioxanonane, +3,6,9-trioxaundecane, +5,8,11-trioxapentadecane, and +2,5,8,11,14-pentaoxapentadecane, or for 2-(2-ethoxyethoxy)ethanol + 2,5,8-trioxanonane, +3,6,9-trioxaundecane, and +5,8,11-pentaoxapentadecane have been obtained from densities measured with and Anton-Paar DMA 602 vibrating-tube densimeter.

The V^E values are usually negative indicating that interactions between unlike molecules are predominant over other effects. The investigated mixtures behave similar to those with 2-methoxyethanol, 2-ethoxyethanol or 2-butoxyethanol and the same oxaalkanes.

Keywords: Experimental; Excess volume; 2-(2-alkoxyethoxy)ethanol; *n*-Polyether

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 because they are increasingly used as additives to gasoline owing to their octane-enhancing and pollution reducing properties [1,2]. Both groups may belong to the same molecule used to build hydroxyethers, which are nonionic amphiphile molecules, and consequently are very effective surfactants with a large number of applications [3–6].

Theoretically, solutions involving oxaalkanes are of high interest because of the possibility of studying a number of effects (e.g. steric or proximity effects, cyclization) on the interactions present in the mixture. On the other hand, those systems where one of the components is a hydroxyether are also very interesting because the intramolecular effects between their –OH and –O– groups are of great importance [7–9].

The OH/O Project is part of a general program, the so-called TOM Project [10,11], in which mixtures containing the –O– and/or the –OH groups are investigated in order to characterize the interactions where these groups participate. Special attention is paid to intra- and intermolecular effects related to the presence of the O and/or OH groups in the same or different molecules.

Particularly, for systems containing alkoxyethanols, we have contributed principally to this project by reporting a large quantity of measurements on the vapor–liquid equilibria (VLE), liquid–liquid equilibria (LLE), molar excess enthalpies, H^E, molar excess heat capacities at constant pressure, C_p^E and molar excess volumes, V^E [12–25].

On the other hand, alkoxyethanol + alkane mixtures have been successfully characterized [9] in the framework of DISQUAC [10,11], a purely physical model based on the rigid lattice theory developed by Guggenheim [26]. Because in terms of DISQUAC, $V^E = 0$, we have also applied [27] the ERAS model [28] to such solutions. As it is known, ERAS combines the real-association solution model [29–32] with

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a physical contribution expressed by the Flory equation of state [33]. It makes possible to predict simultaneously H^E and V^E. It is remarkable that ERAS can be applied only to mixtures where association is expected (1-alkanol + alkane [34], 1-alkanol + amine [35]). Notable is the lack of a systematic treatment of 1-alkanol + *n*-polyether mixtures by ERAS, which underlines the difficulty in studying systems where the –O– and –OH groups are involved. Indeed, only solutions of 1-propanol with 2,5,8-trioxanonane, or with 2,5,8,11-tetraoxadodecane have been studied in terms of ERAS with the assumption that the ethers are self-associated [36]. In contrast, a complete treatment of 1-alkanol + *n*-polyether systems is available in terms of DISQUAC [37].

In addition, mixtures of two alkoxyethanols have been studied [38] in the framework of the Flory theory [33].

More recently, we have also presented V^E data at 298.15 K and atmospheric pressure for 2-alkoxyethanol + *n*-polyether mixtures [39]. As continuation we report now V^E data, at the same conditions, for 2-(2-methoxyethoxy)ethanol or 2-(2-butoxyethoxy)ethanol + 2,5-dioxahexane, +2,5,8-trioxanonane, +3,6,9-trioxaundecane, +5,8,11-trioxapentadecane or +2,5,8,11,14-pentaoxapentadecane, and for 2-(2-ethoxyethoxy)ethanol+2,5,8-trioxanonane, +3,6,9-trioxaundecane, or +5,8,11-trioxapentadecane. This database will be useful in order to investigate the reliability of the ERAS model to represent alkoxyethanol + *n*-polyether systems.

2. Experimental

2.1. Materials

Chemicals were provided by Fluka: 2-(2-methoxyethoxy) ethanol, 2-(2-ethoxyethoxy)ethanol and 2-(2-butoxyethoxy) ethanol, 5,8,11-trioxapentadecane, 2,5,8,11,14-pentaoxapentadecane (all of them purum >98 mol%); 2,5-dioxahexane (puriss ≥99.5 mol%), 2,5,8-trioxanonane and 3,6,9-trioxaundecane (puriss p.a. >99.5 mol%) were used after being carefully dried with molecular sieve (Union Carbide type 4 Å beads, from Fluka). Densities of pure components measured at 298.15 K and atmospheric pressure are listed in Table 1. Good agreement is found between our data and those reported in the literature.

2.2. Apparatus and procedure

An Anton-Paar DMA 602 vibrating-tube densimeter [40,41] 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. The error in τ is $\Delta\tau = \pm 5$ ns, and hence $|\Delta\tau/\tau| = 1.4 \times 10^{-6}$. This gives a resolution in density of $|\Delta\rho/\rho| = 6 \times 10^{-6}$, apart from errors due to calibration and the density of the reference liquids. All the measuring operations and calculations were under computer control.

Table 1
Densities, ρ, of pure compounds at 298.15 K and atmospheric pressure

Compound	ρ (298.15 K)	
	This work	Literature
2-(2-Methoxyethoxy)ethanol	1.01539	1.0167 [47]; 1.0154 [16] 1.01591 [48]; 1.0164 [49]
2-(2-Methoxyethoxy)ethanol	0.9845	0.98468 [16]; 0.9841 [48]
2-(2-Butoxyethoxy)ethanol	0.94898	0.9479 [49]; 0.94869 [50]
2,5-Dioxahexane	0.86162	0.8637 [47]; 0.8609 [50] 0.86132 [51]
2,5,8-Trioxanonane	0.93908	0.9384 [47]; 0.9394 [51] 0.93873 [52]
3,6,9-Trioxaundecane	0.90106	0.902 [47]; 0.9021 [53]
5,8,11-Trioxapentadecane	0.8788	0.871 [47]; 0.878 [54]
2,5,8,11,14-Pentaoxapentadecane	1.006485	1.0063 [51]; 1.0062 [55]

Before each series of measurements the instrument was calibrated with doubly distilled and degassed water and “vacuum”. The inaccuracy in the determination of density ρ is believed to be less than $\pm 2 \times 10^{-2}\ \mathrm{kg\,m^{-3}}$. Hexane and acetone or ethanol were used for rinsing the cell tube between measurements. More details are given elsewhere [42]. The temperature was measured by a quartz thermometer. The densimeter was thermostated to ±0.003 K and measurements were carried out at 298.15 K and atmospheric pressure.

Binary mixtures were prepared by mass in small vessels of about 10 $\mathrm{cm^3}$. 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 [43].

The excess molar volumes, V^E, were calculated from the densities of the pure liquids and their mixtures. The inaccuracy in V^E is believed to be less than $(\pm 0.01 V^E_M + 0.005\ \mathrm{cm^3\,mol^{-1}})$, where V^E_M denotes the maximum or minimum experimental value of the V^E with respect to the mole fraction for a given system.

3. Results and discussion

The results of V^E as a function of mole fraction of the alkoxyethanol, x_1, are collected in Table 2. The data were fitted by unweighted least-squares polynomial regression to the equation:

$$V^E\ (\mathrm{cm^3\,mol^{-1}}) = x_1(1 - x_1)\sum_{i=1}^{k} A_i(2x_1 - 1)^{i-1} \qquad (1)$$

The number of coefficients, k, used in Eq. (1) for each mixture was determined by applying an F-test [44] at the 95% confidence level. Table 3 lists the parameters A_i obtained in the regression, together with the standard deviations, σ,

Table 2
Molar excess volumes, V^E, for 2-(2-alkoxyethoxy)ethanol (1) + *n*-poly ether (2) systems at 298.15 K and atmospheric pressure

x_1	V^E (cm^3 mol^{-1})
2-(2-methoxyethoxy)ethanol (1) + 2,5-dioxahexane (2)	
0.1100	−0.1841
0.2048	−0.2906
0.3073	−0.3626
0.4037	−0.3952
0.4964	−0.3969
0.6141	−0.3627
0.7097	−0.3051
0.7973	−0.2377
0.8892	−0.1411
2-(2-methoxyethoxy)ethanol (1) + 2,5,8-trioxanonane (2)	
0.0977	−0.0599
0.1902	−0.1039
0.1912	−0.1040
0.2788	−0.1357
0.3686	−0.1560
0.4763	−0.1672
0.5759	−0.1647
0.6758	−0.1503
0.7814	−0.1189
0.8862	−0.0739
2-(2-methoxyethoxy)ethanol (1) + 3,6,9-trioxaundecane (2)	
0.1100	−0.1064
0.2063	−0.1731
0.3004	−0.2230
0.3934	−0.2526
0.4999	−0.2701
0.6003	−0.2614
0.7014	−0.2326
0.8002	−0.1836
0.8984	−0.1085
2-(2-methoxyethoxy)ethanol (1) + 5,8,11-trioxapentadecane (2)	
0.1083	0.0233
0.2083	0.0413
0.3018	0.0555
0.3986	0.0678
0.4964	0.0733
0.5955	0.0734
0.6995	0.0701
0.7990	0.0563
0.8972	0.0344
2-(2-methoxyethoxy)ethanol (1) + 2,5,8,11,14-pentaoxapentadecane (2)	
0.1166	−0.0344
0.2080	−0.0532
0.3089	−0.0708
0.4022	−0.0811
0.5038	−0.0854
0.6022	−0.0847
0.7021	−0.0773
0.8010	−0.0625
0.8982	−0.0369
2-(2-ethoxyethoxy)ethanol (1) + 2,5,8-trioxanonane (2)	
0.1009	−0.0311
0.1989	−0.0531
0.2928	−0.0699
0.3911	−0.0807
0.4935	−0.0850
0.6125	−0.0815
0.6968	−0.0732
0.7925	−0.0575
0.8898	−0.0346
2-(2-ethoxyethoxy)ethanol (1) + 3,6,9-trioxaundecane (2)	
0.1012	−0.0793
0.2019	−0.1401
0.2940	−0.1762
0.3875	−0.1994
0.4962	−0.2098
0.5944	−0.2000
0.6971	−0.1747
0.7946	−0.1343
0.8941	−0.0773
2-(2-ethoxyethoxy)ethanol (1) + 5,8,11-trioxapentadecane (2)	
0.0585	0.017
0.1553	0.036
0.2612	0.057
0.3452	0.062
0.4400	0.066
0.5567	0.067
0.6506	0.063
0.7589	0.057
0.8537	0.042
0.9472	0.018
0.9716	0.009
2-(2-butoxyethoxy)ethanol (1) + 2,5-dioxahexane (2)	
0.1044	−0.1308
0.1996	−0.2063
0.3021	−0.2526
0.5104	−0.2598
0.5427	−0.2506
0.7025	−0.1893
0.8212	−0.1222
0.8942	−0.0713
2-(2-butoxyethoxy)ethanol (1) + 2,5,8-trioxanonane (2)	
0.0954	−0.0082
0.1976	−0.0138
0.2886	−0.0175
0.3979	−0.0227
0.4936	−0.0234
0.5934	−0.0222
0.6989	−0.0212
0.7971	−0.0165
0.8920	−0.0106
2-(2-butoxyethoxy)ethanol (1) + 3,6,9-trioxaundecane (2)	
0.1071	−0.0892
0.2017	−0.1449
0.2920	−0.1855
0.3924	−0.2111
0.4875	−0.2171
0.5971	−0.2068
0.6959	−0.1809
0.7915	−0.1414
0.8592	−0.1020
0.8903	−0.0833
2-(2-butoxyethoxy)ethanol (1) + 5,8,11-trioxapentadecane (2)	
0.1024	−0.0185
0.1982	−0.0358
0.2907	−0.0494
0.3918	−0.0616
0.4904	−0.0679
0.5899	−0.0693

Table 2 (*continued*)

x_1	V^E (cm^3 mol^{-1})
0.6944	−0.0643
0.7933	−0.0513
0.8920	−0.0309
2-(2-butoxyethoxy)ethanol (1) + 2,5,8,11,14-pentaoxapentadecane (2)	
0.1091	0.023
0.2037	0.039
0.3038	0.051
0.3960	0.056
0.5032	0.057
0.5983	0.056
0.7041	0.047
0.8014	0.031
0.8075	0.014

defined by

$$\sigma(V^E)\ (\mathrm{cm^3\,mol^{-1}}) = \left[\sum \frac{(V^E_{\mathrm{calc}} - V^E_{\mathrm{exp}})^2}{N-k}\right]^{1/2} \qquad (2)$$

where N stands for the number of direct experimental values. For all the mixtures $\sigma(V^E)/|V^E_M| < 0.03$ in accordance with the precision attainable with the instrument used. A graphical representation of the experimental results and smoothing curves from Eq. (1) is shown in Figs. 1 and 2. Our data for the 2-(2-methoxyethoxy)ethanol + 2,5-dioxahexane system are in good agreement with those available in the literature [45] (Fig. 1). No more data have been found in the literature for comparison.

For the investigated mixtures, V^E is the result of several opposing effects. Changes in the self-association (inter- or intramolecular [9]) of alkoxyethanols and physical interactions between alkoxyethanol molecules, or between ether molecules lead to increased V^E. On the contrary, free volume effects, interstitial accommodation or interactions between unlike molecules decrease V^E. We note that for these systems, V^E is usually negative and conclude that the interactions between unlike molecules are predominant over other effects. In spite of the great complexity of the solutions under study, some general trends can be noted:

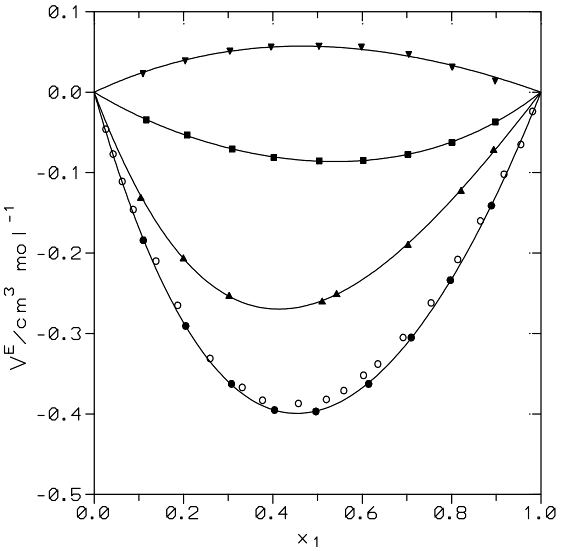

Fig. 1. V^E at 298.15 K and atmospheric pressure for 2-(2-alkoxyethoxy) ethanol (1) + *n*-polyether (2) mixtures. Points, experimental results (this work): 2-(2-methoxyethoxy)ethanol (1) + 2,5-dioxahexane (2) (●); [45] (○); +2,5,8,11,14-pentaoxapentadecane (2) (■); 2-(2-butoxyethoxy)ethanol (1) + 2,5-dioxahexane (2) (▲); +pentaoxapentadecane (2) (▼). Solid lines, calculations with Eq. (1) and coefficients from Table 3.

(i) For a given 2-(2-alkoxyethoxy)ethanol, V^E ($x = 0.5$) varies in the sequence: 2,5,8-trioxanonane > 3,6,9-trioxaundecane < 5,8,11-trioxapentadecane (Table 4). The decrease of V^E when passing from 2,5,8-trioxanonane to 3,6,9-trioxaundecane may be due to larger positive contribution to V^E from the rupture of the dipole–dipole interactions between oxaalkane molecules in the case of 2,5,8-trioxanonane.

In systems with 5,8,11-trioxapentadecane, interactions between unlike molecules are weaker because the –O– atoms are more screened in this ether. In addition,

Table 3
Coefficients A_i and standard deviations, $\sigma(V^E)$ (Eq. (2)), for representation of the V^E data at 298.15 K and atmospheric pressure by Eq. (1)

System	N[a]	A_1	A_2	A_3	A_4	$\sigma(V^E)$ (cm^3 mol^{-1})
2-(2-Methoxyethoxy)ethanol + 2,5-dioxahexane	9	−1.5840	0.2827	−0.103		0.0010
2-(2-Methoxyethoxy)ethanol + 2,5,8-trioxanonane	10	−0.6713	−0.0121	−0.0515	−0.0359	0.0005
2-(2-Methoxyethoxy)ethanol + 3,6,9-trioxaundecane	9	−1.0730	−0.0686	−0.090		0.0012
2-(2-Methoxyethoxy)ethanol + 5,8,11-trioxapentadecane	9	0.2967	0.0829			0.0010
2-(2-Methoxyethoxy)ethanol + 2,5,8,11,14-pentaoxapentadecane	9	−0.3429	−0.0493	−0.0421		0.0006
2-(2-Ethoxyethoxy)ethanol + 2,5,8-trioxanonane	9	−0.34165	−0.0109			0.0003
2-(2-Ethoxyethoxy)ethanol + 3,6,9-trioxaundecane	9	−0.83931	0.0306			0.0012
2-(2-Ethoxyethoxy)ethanol + 5,8,11-trioxapentadecane	11	0.2718	0.0212	0.083		0.002
2-(2-Butoxyethoxy)ethanol + 2,5-dioxahexane	8	−1.0448	0.3796	−0.057		0.0017
2-(2-Butoxyethoxy)ethanol + 2,5,8-trioxanonane	9	−0.0940	−0.0124			0.0007
2-(2-Butoxyethoxy)ethanol + 3,6,9-trioxaundecane	10	−0.8698	0.0480	−0.0288		0.0009
2-(2-Butoxyethoxy)ethanol + 5,8,11-trioxapentadecane	9	−0.27434	−0.07472	0.0159		0.0003
2-(2-Butoxyethoxy)ethanol + 2,5,8,11,14-pentaoxapentadecane	9	0.2278	−0.032			0.003

[a] Number of data.

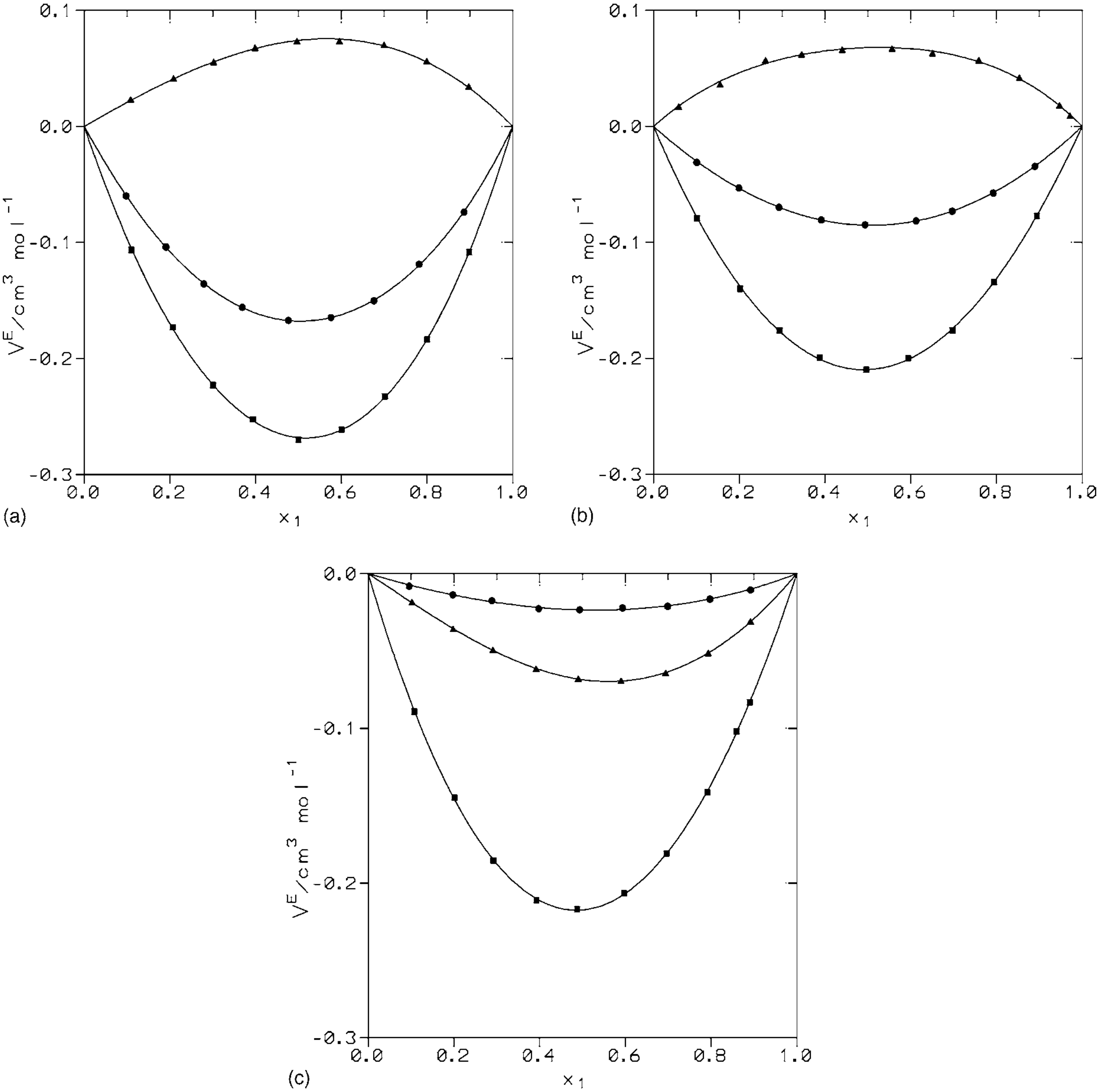

Fig. 2. V^E at 298.15 K and atmospheric pressure for 2-(2-alkoxyethoxy)ethanol (1) + n-polyether (2) mixtures. Points, experimental results (this work): solid lines, calculations with Eq. (1) and coefficients from Table 3. (a) Results for 2-(2-methoxyethoxy)ethanol (1) + 2,5,8-trioxaoctane (2) (●); +3,6,9-trioxaundecane (2) (■); +5,8,11-trioxapentadecane (2) (▲). (b) Results for 2-(2-ethoxyethoxy)ethanol (1) + 2,5,8-trioxaoctane (2) (●); +3,6,9-trioxaundecane (2) (■); +5,8,11-trioxapentadecane (2) (▲). (c) Results for 2-(2-butoxyethoxy)ethanol (1) + 2,5,8-trioxaoctane (2) (●); +3,6,9-trioxaundecane (2) (■); +5,8,11-trioxapentadecane (2) (▲).

Table 4
V^E ($x_1 = 0.5$) at 298.15 K and atmospheric pressure for alkoxyethanol[a] (1) + n-polyether (2) mixtures

	2,5-Dioxahexane	2,5,8-Trioxanonane	3,6,9-Trioxaundecane	5,8,11-Trioxapentadecane	2,5,8,11,14-Pentaoxapentadecane
2-ME	−0.2242 [39]	−0.0944 [39]	−0.1867 [39]	0.0854 [39]	−0.100 [39]
2-EE		−0.0218 [39]	−0.1378 [39]	0.0448 [39]	
2-BEE	−0.1011 [39]	0.0615 [39]	−0.1534 [39]	−0.0936 [39]	0.0823 [39]
2,2-MEE	−0.3960 (this work)	−0.1678 (this work)	−0.2683 (this work)	0.0742 (this work)	−0.0857 (this work)
2,2-EEE		−0.0854 (this work)	−0.2098 (this work)	0.068 (this work)	
2,2-BEE	−0.2612 (this work)	−0.0235 (this work)	−0.2174 (this work)	−0.0686 (this work)	0.057 (this work)

[a] 2-ME, 2-methoxyethanol; 2-EE, 2-ethoxyethanol; 2-BE, 2-butoxyethanol; 2,2-MEE, 2-(2-methoxyethoxy)ethanol; 2,2-EEE, 2-(2-ethoxyethoxy)ethanol; 2,2-BEE, 2-(2-butoxyethoxy)ethanol.

more dipole–dipole interactions between alkoxyethanol molecules are disrupted. Hence, V^{E} increases when passing from 3,6,9-trioxanonane to 5,8,11-trioxapentadecane (Table 4).

(ii) In solutions with 2,5,8-trioxanonane, V^{E} varies in the sequence 2-(2-methoxyethoxy)ethanol < 2-(2-ethoxyethoxy)ethanol < 2-(2-butoxyethoxy)ethanol (Table 4). This trend is probably due to interactions between unlike molecules becoming weaker in the same order.

(iii) To the contrary, in systems with 5,8,11-trioxapentadecane, V^{E} varies as follows: 2-(2-methoxyethoxy) ethanol > 2-(2-ethoxyethoxy)ethanol > 2-(2-butoxyethoxy)ethanol (Table 4). As already mentioned the oxygen atoms in the oxaalkane are here more screened, and this effect leads to a larger number of broken dipole–dipole interactions between hydroxyether molecules. We note that the strength of interactions between 2-(2-alkoxyethoxy)ethanol molecules decreases in the same way [9]. This is clearly shown by the upper critical solution temperatures (UCST) of 2-(2-alkoxyethoxy)ethanol + n-C$_7$ systems. For example, UCST(2-(2-methoxyethoxy)ethanol) = 381.15 K [46]; UCST(2-(2-ethoxyethoxy)ethanol) = 286.98 K [17].

These trends have been also encountered in 2-alkoxyethanol+n-polyether mixtures [39]. Except for 2-methoxyethanol+2,5,8,1,14-pentaoxapentadecane and for 2-butoxyethanol + 5,8,11-trioxapentadecane, for a given polyether, at equimolar composition, V^{E}(2-alkoxyethanol) > V^{E}(2-(2-alkoxyethoxy)ethanol) (Table 4). This behavior may be ascribed to stronger interactions between alkoxyethanol and n-polyether molecules when the former have two –O– groups.

On the other hand, a change in symmetry of the V^{E} curves is observed when passing from 2-alkoxyethanol to 2-(2-alkoxyethoxy)ethanol, as this symmetry strongly depends on the difference in size between the mixture of the components. So, the V^{E} curves are skewed towards high mole fraction of 2-methoxyethanol (the smaller compound) in the solutions with 5,8,11-trioxapentadecane, or with 2,5,8,11,14-pentaoxapentadecane (free volume effects [39]). The V^{E} curves for the corresponding mixtures with 2-(2-methoxyethoxy)ethanol are more symmetrical because the mixture components are of more similar size (Figs. 1 and 2a).

4. Summary

V^{E} data at 298.15 K and atmospheric pressure for 2-(2-methoxyethoxy)ethanol, or 2-(2-butoxyethoxy)ethanol + 2,5-dioxahexane, +2,5,8-trioxanonane, +3,6,9-trioxaundecane, +5,8,11-trioxapentadecane, or +2,5,8,11,14-pentaoxapentadecane, and for 2-(2-ethoxyethoxy)ethanol + 2,5,8-trioxanonane; +3,6,9-trioxaundecane or +5,8,11-trioxapentadecane have been reported. These mixtures behave similar to those containing the same oxaalkanes and 2-methoxyethanol, 2-ethoxyethanol or 2-butoxyethanol.

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