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Thermodynamic properties of *n*-alkoxyethanols + organic solvent mixtures
XIII. Application of the Flory theory to 2-methoxyethanol + *n*-alkoxyethanols systems

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Abstract

The Flory theory has been applied to the following binary mixtures: 2-methoxyethanol (2ME) + 2-ethoxyethanol (2EE), or + 2-butoxyethanol (2BE), and + 2-(2-methoxyethoxy)ethanol(22MEE), +2-(2-ethoxyethoxy)ethanol (22EEE), or + 2-(2-buthoxyethoxy)ethanol (22BEE).

For pure compounds, the coefficients of thermal expansion α and isothermal compressibility K_T were estimated in order to compute the Flory characteristic parameters, pressure p_i^* and volume v_i^*.

For each mixture, the energetic parameter χ_{12} was fitted to excess enthalpy data H^E at 298.15 K and used to predict correctly the corresponding excess volume V^E. The variation of χ_{12} versus the number of C atoms + $-$O$-$ groups in alkoxyethanols is similar to that found previously for 1-alkanol + 1-alkanol mixtures.

Keywords: Flory theory; Alkoxyethanols; Intramolecular bonds; Self-association; Dipolar interactions

1. Introduction

The OH/O Project is part of a general program, the so-called TOM Project [1,2], in which mixtures containing the oxygen (–O–) and/or the hydroxyl (–OH) groups are studied in order to characterise their interactions. Special attention is paid to intra and intermolecular effects, related to the presence of –O– and/or –OH groups in the same or different molecules.

Mixtures containing hydroxyethers are very important from a theoretical point of view, not only because of their self-association [3,4], but also due to the strong intramolecular effects produced by the presence of –O– and –OH groups in the same molecule (hydroxyether) [3–5]. On the other hand, dipole moments of alkoyethanols are higher than those of *n*-alkanols [6], what suggests the existence of strong dipole-dipole interactions [4,7–9]. In the framework of the TOM project, our final purpose is the characterisation of these systems in terms of the DISQUAC group contribution model [1,2].

With this purpose, up to now we have contributed to this part of the OH/O project reporting experimental data at 298.15 K on H^E [4,10–12], V^E [12–16], excess

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Nomenclature

H	enthalpy
K_T	isothermal compressibility coefficient
p	pressure
s	number of contacts of a molecule
S_{12}	geometric parameter in the Flory theory
T	temperature
v,V	volume
x	mole fraction
Greek symbols	
α	isobaric thermal expansivity
χ_{12}	energetic parameter in the Flory theory
φ	segment fraction in the Flory theory
θ	site fraction in the Flory theory
Superscripts	
E	excess value
–	reduced value
$*$	characteristic value
Subscripts	
i	component i

heat capacities at constant pressure [12–14], liquid–liquid equilibria [7–9] and vapour–liquid equilibria [17,18]. More experimental work is in progress.

The aim of this paper is to analyse the ability of the Flory theory [19,20] to represent 2-methoxyethanol+ alkoxyethanol mixtures, which show low V^E and H^E values [12,21–23], as a consequence of the similar chemical nature of the components. It is remarkable that the Flory theory has been applied successfully, not only to mixtures containing a weakly polar compound and an inert compound (e.g. linear monoether+ *n*-alkane [24–26]), but also to 1-alkanol + 1-alkanol systems [27].

2. Theory

According to the Flory theory [19,20], a molecule consists of n segments (isomeric portions), each having s intermolecular contact sites which can interact with neighbouring sites. The molar volume v of a pure liquid is given by

$$v = r \cdot v' = v^* \cdot \bar{v} \tag{1}$$

where v' is the volume of a mole of segments, v^* the characteristic volume and $\bar{v}$ the reduced volume. At temperature T, the value of the reduced volume $\bar{v}$ can be calculated from the coefficient of thermal expansion α using the expression

$$\bar{v} = \left(\frac{4T\alpha + 3}{3T\alpha + 3}\right)^3 \tag{2}$$

At zero pressure, the reduced volume $\bar{v}$ and the reduced temperature $\bar{T}$ satisfy the equation

$$\bar{T} = \frac{\bar{v}^{1/3} - 1}{\bar{v}^{4/3}} \tag{3}$$

The characteristic temperature T^* and the characteristic pressure p^* can be obtained from the relations

$$T^* = \frac{T}{\bar{T}} \tag{4}$$

$$p^* = \left(\frac{\alpha}{K_T}\right) T\bar{v}^2 \tag{5}$$

For a mixture, it is assumed that Eq. (3) is valid and that the reduced temperature is

$$\bar{T} = \frac{\varphi_1 p_1^* \bar{T}_1 + \varphi_2 p_2^* \bar{T}_2}{\varphi_1 p_1^* + \varphi_2 p_2^* - \varphi_1 \theta_2 \chi_{12}} \tag{6}$$

where φ_1 and φ_2 are the segment fractions defined by

$$\varphi_2 = 1 - \varphi_1 = \frac{r_2 x_2}{r_1 x_1 + r_2 x_2} \tag{7}$$

and the site fractions θ_2 is defined by

$$\theta_2 = \frac{s_2 \varphi_2}{s_1 \varphi_1 + s_2 \varphi_2} \tag{8}$$

To compute Eq. (8), it is assumed molecules are spherical, so that the geometrical parameter $S_{12} = s_1/s_2$ is estimated using next expression:

$$S_{12} = \frac{s_1}{s_2} = \left(\frac{v_2^*}{v_1^*}\right)^{1/3} \tag{9}$$

In Eq. (6), χ_{12} is a constant which characterises the difference between the energy of interaction among sites on neighbouring molecules of different species and the average of the interaction energies in pure liquids.

It is usual to treat χ_{12} as an adjustable parameter, obtaining its value by fitting the theoretical expression for H^{E}, Eq. (10), to experimental results.

$$H^{\mathrm{E}} = x_1 p_1^* v_1^* \left(\frac{1}{\bar{v}_1} - \frac{1}{\bar{v}}\right) + x_2 p_2^* v_2^* \left(\frac{1}{\bar{v}_2} - \frac{1}{\bar{v}}\right) + \frac{x_1 v_1^* \theta_2 \chi_{12}}{\bar{v}} \tag{10}$$

The expression for V^{E} is

$$V^{\mathrm{E}} = \left(x_1 v_1^* + x_2 v_2^*\right)\left(\bar{v} - \varphi_1 \bar{v}_1 - \varphi_2 \bar{v}_2\right) \tag{11}$$

In Eqs. (10) and (11), $\bar{v}$ is the reduced volume of the mixture which can be evaluated from Eq. (3).

3. Estimation of the energetic parameter

3.1. Thermal coefficients of pure components

In order to apply the Flory theory, it is necessary to determine the characteristic parameters of pure compounds (v_i^*, p_i^* and T_i^*, $i = 1, 2$). With this purpose, their thermal coefficients are needed (see Eqs. (2) and (5)). Data on α and K_{T} at 298.15 K for pure hydroxyethers are available in literature [6,28–43]. However, they are not sure because differ considerably. The values used in the present work were estimated according to the following simple rules:

1. Alkoxyethanols must show higher expansivities than their corresponding homomorphic 1-alkanols because the later are more self-associated [4,8,9].
2. The compressibility of 1-alkanol is higher than the corresponding of the homomorphic alkoxyethanol due to the intramolecular bonds in the later [3–5].

Final values are listed in Table 1.

3.2. Fitting procedure

The energetic parameter χ_{12} was obtained for each system by means of a Marquardt algorithm [44] which minimises the objective function

$$X^2(\chi_{12}) = \sum \left(H^{\mathrm{E}}_{\mathrm{Flory}} - H^{\mathrm{E}}_{\mathrm{Exp}}\right)^2 \tag{12}$$

The calculated χ_{12} are listed in Table 2. Due to the rather low H^{E} of the present mixtures, when developing calculations, caution should be exercised with the used values of v_i^*, p_i^* and T_i^*. As a matter of fact, some problems could appear at high dilution because of the rounded values of v_i^*, p_i^* and T_i^*. The characteristic parameters directly used in this work are listed in Table 1.

4. Results and discussion

Results are presented along Tables 2 and 3, and Figs. 1–6. For the sake of clarity, Tables 2 and 3 include standard deviations defined as

$$\sigma(F^{\mathrm{E}}) = \sqrt{\frac{1}{N} \sum \left(F^{\mathrm{E}}_{\mathrm{exp}} - F^{\mathrm{E}}_{\mathrm{Flory}}\right)^2} \tag{13}$$

Table 1
Physical constants and Flory characteristic parameters of pure components

Component[a]	v[b] (cm^3/mol)	α_i[c] (K^{-1})	$K_{\mathrm{T},i}$[c] (Pa^{-1})	p_i^*[d] (J cm^{-3})	v_i^*[e] (cm^3/mol)
2ME	79.25	9.6×10^{-4}	8.0×10^{-10}	549.6	63.94
2EE	97.41	9.3×10^{-4}	7.7×10^{-10}	547.6	78.99
2BE	131.86	8.7×10^{-4}	7.3×10^{-10}	529.2	108.04
22MEE	118.2	8.8×10^{-4}	7.4×10^{-10}	529.9	96.68
22EEE	136.37	8.6×10^{-4}	7.1×10^{-10}	536.0	111.94
22BEE	171.15	8.2×10^{-4}	6.7×10^{-10}	533.9	141.49

[a] 2-Methoxyethanol (2ME); 2-ethoxyethanol (2EE); 2-butoxyethanol (2BE); 2-(2-methoxyethoxy)ethanol (22MEE); 2-(2-ethoxyethoxy)ethanol (22EEE); 2-(2-buthoxyethoxy)ethanol (22BEE).

[b] From [6].

[c] Values estimated in this work.

[d] Calculated using Eq. (5).

[e] Calculated using Eq. (2).

Table 2
Comparison of the experimental results [12,21] for H^E at 298.15 K with values calculated from the Flory theory using the χ_{12} parameters determined in this work[a]

Mixture[b]	X_{12} (J cm^{-3})	$N(H^E)$[c]	$H^E(x = 0.5)$ (J/mol)		$\sigma(H^E)$ (J/mol)	
			Flory	Experimental[d]	Flory	Experimental[d]
2ME + 2EE	2.231	20	39.4	39.4	0.5	0.3
2ME + 2BE	10.961	21	210.7	210.5	5.6	1.4
2ME + 22MEE	−0.660	23	−13.8	−13.4	0.7	0.6
2ME + 22EEE	−0.151	25	−5.2	−5.3	1.2	0.6
2ME + 22BEE	5.516	21	109.6	107.8	6.6	0.7

[a] $\sigma(H^E)$ is the standard deviation Eq. (13).

[b] For symbols, see Table 1.

[c] Number of experimental points.

[d] Calculated from Redlich–Kister correlation.

where N is the number of data points for each system, and F is H (enthalpy) or V (volume).

We note that $\sigma(H^E)$ increases along a homologous series for systems having large differences in chain length (see Table 2). This probably reflects a weakness of the present treatment which essentially assumes that sites of specific interactions associated with different parts of a molecule can be averaged over the molecule and that a single energy parameter can be used to describe the interactions between unlike molecules in a mixture [27]. However, it is remarkable that if χ_{12} is fitted to H^E data of a given mixture, it is possible to predict correctly the corresponding V^E (Table 3). This confirms that the Flory theory is useful in estimating V^E from H^E for mixtures involving hydrogen-bonded molecules.

Fig. 4 plots χ_{12} versus the number of C atoms and –O– groups in alkoxyethanols. The relative variation is similar to that of H^E and V^E (Figs. 5 and 6). So, $\chi_{12}[CH_3{-}(CH_2)_n{-}O{-}CH_2{-}CH_2OH] > \chi_{12}[CH_3{-}(CH_2)_n{-}O{-}CH_2{-}CH_2{-}O{-}CH_2OH]$. 1-Alkanols+1-alkanols mixtures behave similarly (Figs. 5 and 6).

It is interesting to compare H^E of the systems under study with those of mixtures containing the corresponding homomorphic 1-alkanols. So, at equimolar composition and 298.15 K, H^E[2-methoxyethanol+2,2-ethoxyethoxyethanol] = −5.3 J/mol [21] < H^E [1-butanol + 1-octanol] = 103.8 J/mol [27]. In the same way, H^E[2-methoxyethanol + 2,2-butoxyethoxyethanol] = 107.8 J/mol [21] <H^E[1-butanol+1-decanol] = 201.3 J/mol [27]. Such differences underline the importance of intramolecular H-bonds

Table 3
Comparison of the experimental results for V^E at 298.15 K with values calculated from the Flory theory using the χ_{12} parameters listed in Table 2[a]

Mixture[b]	$N(V^E)$[c]	$V^E(x = 0.5)$ (cm^3/mol)		$\sigma(V^E)$ (cm^3/mol)		Data from ref.
		Flory	Experimental[d]	Flory	Experimental[d]	
2ME + 2EE	9	0.0236	0.0087	0.0113	0.0002	[12,22]
2ME + 2BE	9	0.1307	0.1239	0.0051	0.0009	[12,22]
2ME + 22MEE	9	−0.0038	−0.0235	0.016	0.0003	[12,22]
2ME + 22MEE	20	−0.0038	−0.0109	0.0044	0.0001	[23]
2ME + 22EEE	21	−0.0047	−0.0223	0.0141	0.0002	[23]
2ME + 22BEE	20	0.0544	0.0614	0.007	0.0008	[23]

[a] $\sigma(V^E)$ is the standard deviation Eq. (13).

[b] For symbols, see Table 1.

[c] Number of experimental excess volume points.

[d] Calculated from Redlich–Kister correlation.

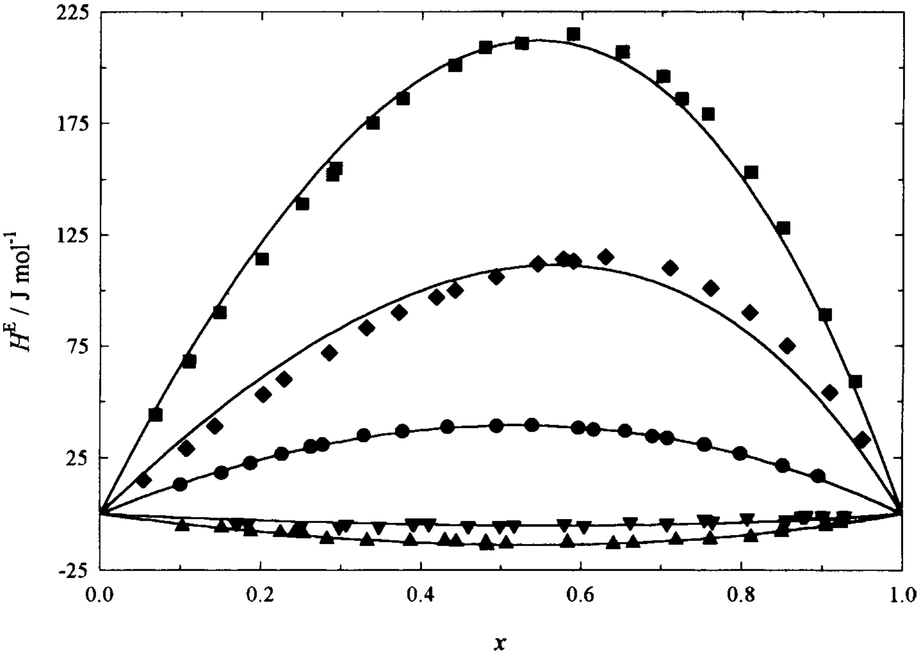

Fig. 1. H^E for mixtures between alkoxyethanols at 298.15 K vs. the mole fraction of 2ME. (Points) experimental data [12,21]: (●) 2ME + 2EE; (■) 2ME + 2BE; (▲) 2ME + 22MEE; (▼) 2ME + 22EEE; (◆) 2ME + 22BEE. Solid curves, results from the Flory theory using χ_{12} listed in Table 2.

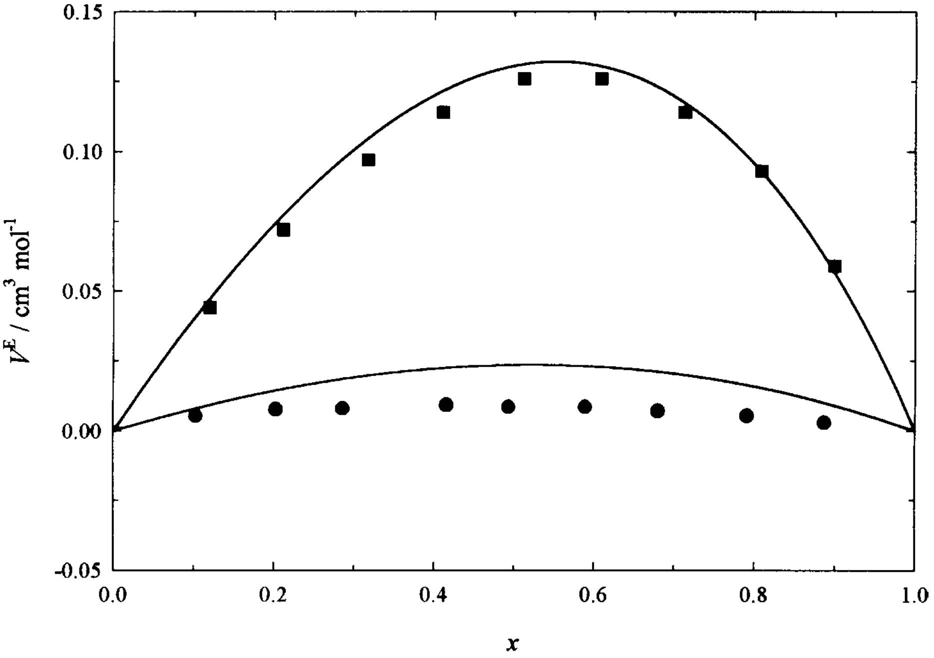

Fig. 2. V^E for mixtures between alkoxyethanols at 298.15 K vs. the mole fraction of 2ME. (Points) experimental data [12,22]: (●) 2ME + 2EE; (■) 2ME + 2BE. Solid curves, results from the Flory theory using χ_{12} listed in Table 2.

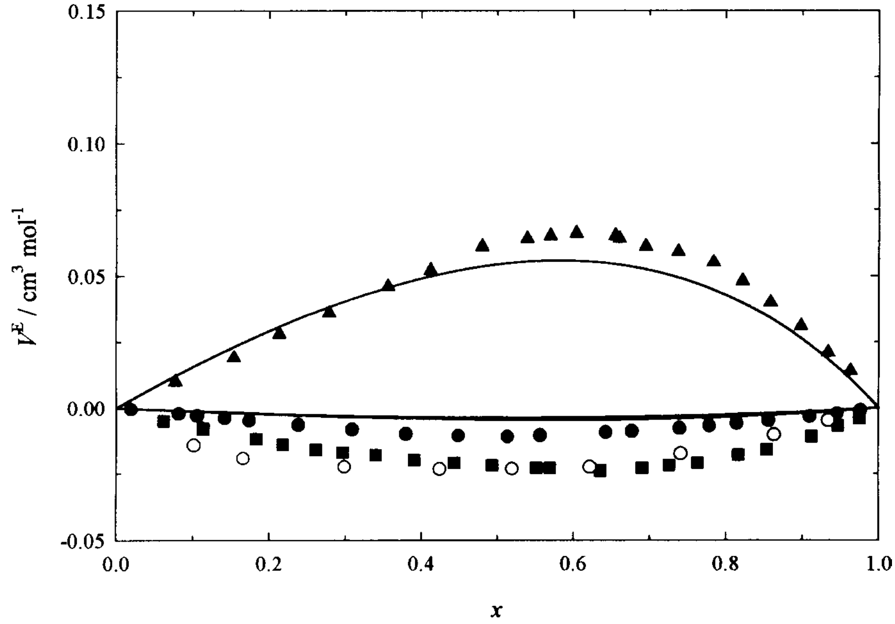

Fig. 3. V^E for mixtures between alkoxyethanols at 298.15 K vs. the mole fraction of 2ME. (Points) experimental data: (●) 2ME + 22MEE [23]; (○) 2ME + 22MEE [12,22]; (■) 2ME + 22EEE [23]; (▲) 2ME + 22BEE [23]. Solid curves, results from the Flory theory using χ_{12} listed in Table 2.

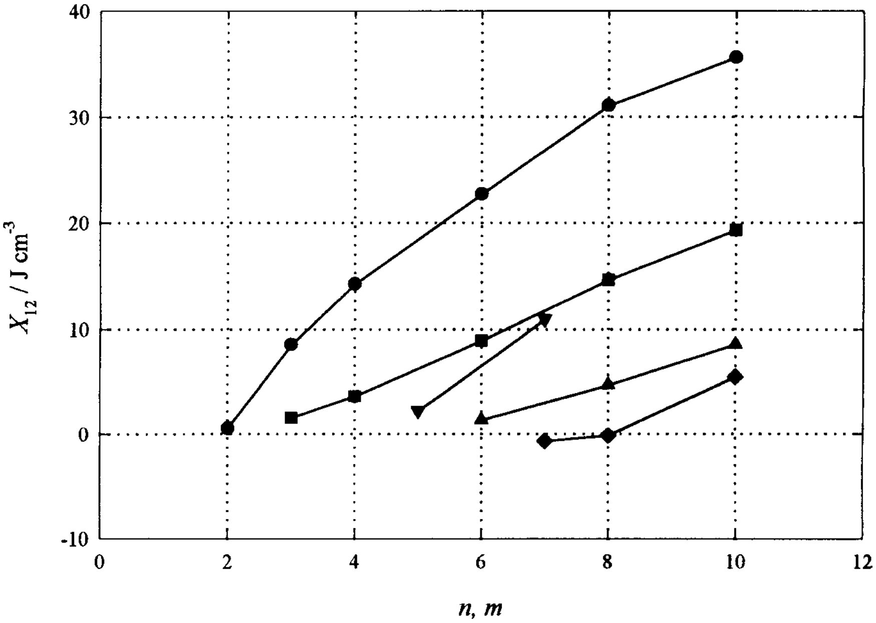

Fig. 4. χ_{12} at 298.15 K for 1-alkanol + 1-alkanol [27] and alkoxyethanol + alkoxyethanol [this work] mixtures vs. n, the number of C atoms in the 1-alkanol, or m, the number of C atoms and –O– groups in the alkoxyethanol: (●) methanol + 1-alkanols; (■) ethanol + 1-alkanols; (▲) 1-butanol + 1-alkanols; (▼) 2ME + 2EE, +2BE; (◆) 2ME + 22MEE + 22EEE, +22BEE.

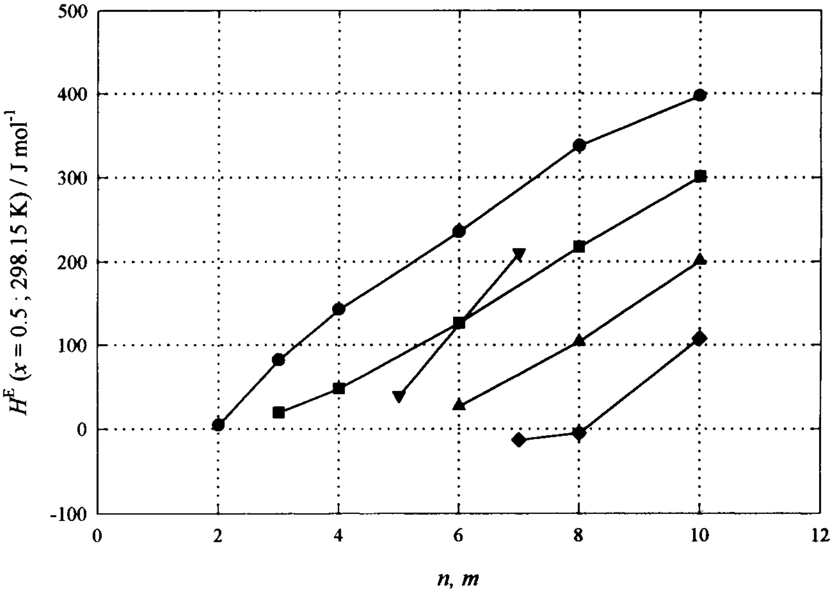

Fig. 5. Experimental H^E at 298.15 K and equimolar composition for 1-alkanol + 1-alkanol [27] or alkoxyethanol + alkoxyethanol [12,21] mixtures vs. n, the number of C atoms in the 1-alkanol, or m, the number of C atoms and –O– groups in the alkoxyethanol: (●) methanol + 1-alkanols; (■) ethanol + 1-alkanols; (▲) 1-butanol + 1-alkanols; (▼) 2ME + 2EE, +2BE; (◆) 2ME + 22MEE, +22EEE, +22BEE.

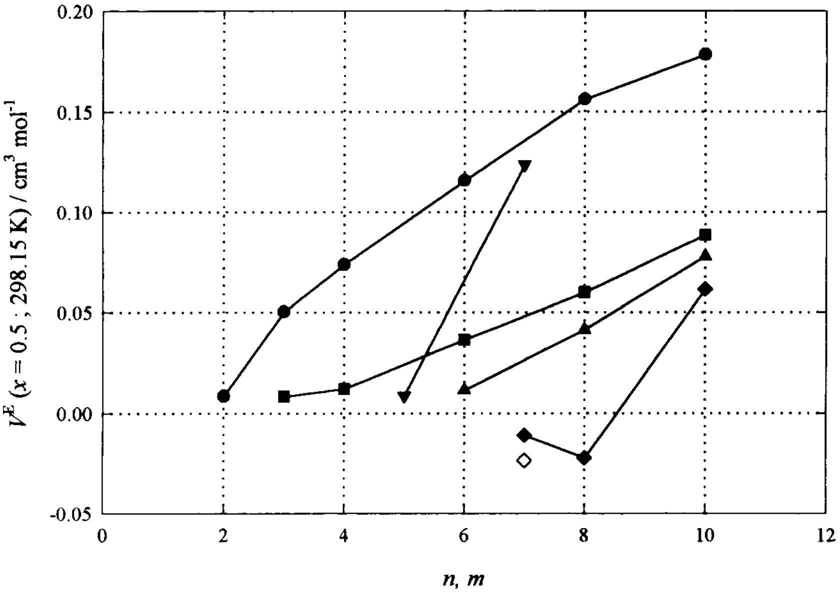

Fig. 6. Experimental V^E at 298.15 K and equimolar composition for 1-alkanol + 1-alkanol [27] or alkoxyethanol + alkoxyethanol mixtures vs. n, the number of C atoms in the 1-alkanol, or m, the number of C atoms and –O– groups in the alkoxyethanol: (●) methanol + 1-alkanols; (■) ethanol + 1-alkanols; (▲) 1-butanol + 1-alkanols; (▼) 2ME + 2EE, +2BE [12,22]; (◇) 2ME + 22MEE [12,22]; (◆) 2ME + 22MEE, +22EEE, +22BEE [23].

in those systems containing hydroxyethers with two –O– groups. Note that H^E[2-methoxyethanol + 2-butoxyethanol] > H^E[2-methoxyethanol + 2, 2-butoxyethoxyethanol] because the larger number of –O– groups in 2,2-butoxyethoxyethanol leads to larger number of inter/intramolecular H-bonds created.

On the contrary, it is expected that H^E[2-methoxyethanol + 2-ethoxyethanol] > H^E[1-butanol + 1-pentanol] and H^E[2-methoxyethanol + 2-butoxyethanol] > H^E[1-butanol + 1-heptanol] (Fig. 5). It suggests that the increase of the dipolar interactions above mentioned is more important.

The observed increase in H^E with the size of the second component in 2-methoxyethanol+ alkoxyethanol mixtures may be attributed to the more inert character of the longer hydroxyethers, as well as their –O– groups are more sterically hindered to form inter/intramolecular H-bonds.

5. Conclusions

Energetic parameters χ_{12} for 2-methoxyethanol+ alkoxyethanol systems calculated from H^E data at 298.15 K are reported. It is shown that they are useful to predict the corresponding V^E. The variation of χ_{12} versus the number of C atoms + –O– groups in alkoxyethanols is similar to that found previously for 1-alkanol + 1-alkanol mixtures.

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