Thermochimica Acta 476 (2008) 20–27

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Thermodynamics of mixtures containing alkoxyethanols Part XXVII. Predictions on isobaric thermal expansion coefficients, compressibilities and speeds of sound from the Flory theory

Juan Antonio González[a,*], Ismael Mozo[a], Isaías García De La Fuente[a], José Carlos Cobos[a], Nicolás Riesco[b]

[a] G.E.T.E.F., Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Valladolid, 47071 Valladolid, Spain
[b] Department of Earth Science and Engineering, Imperial College London, Exhibition Road, London SW7 2AZ, UK

ARTICLE INFO

Article history:
Received 27 June 2008
Received in revised form 15 July 2008
Accepted 15 July 2008
Available online 23 July 2008

Keywords:
Flory theory
Isobaric expansion coefficient
Compressibility
Speed of sound
Orientational effects
Structural effects

ABSTRACT

The Flory model is applied to predict the isobaric expansion coefficients, α_P, isentropic, κ_S, and isothermal, κ_T, compressibilities and speeds of sound, u, of the highly complex mixtures: hydroxyether + alkane, + dibutylether, + 1-butanol or + 2-methoxyethanol, 1-alkanol + alkane, and 1-alkanol + dibutylether. Predictions were obtained using the energetic parameter, χ_{12}, determined from values of excess enthalpies, H^E, and from values of the excess isochoric internal energies, U_V^E, at equimolar composition. No meaningful differences exist between such predictions. Deviations between experimental and calculated values are lower than 2% for mixtures containing alkoxyethanols. Poorer results are obtained for 1-alkanol + dibutylether mixtures with deviations up to 5%. It is shown that predictions on α_P, κ_S, κ_T, and u essentially depend on structural effects and not on the orientational effects present in the studied mixtures. Results are improved using χ_{12} values fitted to molar excess volumes. In this case, deviations are similar to those obtained from semiempirical models as free length theory, collision factor theory, or Nomoto or Junjie equations.

1. Introduction

During many years, order creation and order-destruction processes in liquid mixtures involving molecules which do not form hydrogen bonds have been investigated by measuring first order thermodynamic excess functions, such as H^E and V^E, and other second order quantities like C_P^E, isobaric molar excess heat capacity, $(\partial V^E/\partial T)_P$, or $-(\partial V^E/\partial P)_T$ of systems of the type B + C_n [1–7]. B is usually a non-polar or slightly polar compound, with spherical or plate like shape (e.g., benzene, toluene, cyclohexane, or a highly branched alkane), and C_n is an alkane. The main conclusion of these studies is the existence of a short-orientational order between long chain *n*-alkane molecules in the pure state, which does not exist in short chain or branched alkanes. B molecules act as order breakers when are mixed with long alkanes, and this leads, e.g., to an extra positive contribution to H^E (the so-called Patterson's effect [8,9]) and to abnormally negative C_P^E values as the mentioned order in the long alkanes rapidly decreases when the temperature increases [10]. The breaking ability of each molecule depends on its structure. So, benzene has a larger ability than *p*-xylene to break the orientational order of long chain *n*-alkanes. However, the mentioned order-destruction can be counterbalanced by compensatory order between the molecules of the mixture. This is the case of 1-chloronaphthalene + *n*-alkane systems, which show a net creation of order [11,12]. From a theoretical point of view, the Flory theory [13,14] has been used in the study of order-destruction and order creation processes [6,8,15–18]. As a basic assumption of this model is random mixing [13] (i.e., any order effects are ignored), the thermodynamic properties of B + branched alkanes systems are well represented by the theory. In contrast, differences between experimental and calculated values are observed for those mixtures including long chain *n*-alkanes, which has been ascribed to the mentioned orientational order in such alkanes.

Recently, we have shown that the Flory model is also useful to investigate orientational effects in highly complex mixtures (e.g., 2-alkoxyethanol + 1-butanol) by examining the dependence of the energetic parameter with the concentration [19]. The purpose of this work is to study the ability of the model to predict properties such as isobaric expansion coefficient, α_P isentropic, κ_S, or isothermal, κ_T compressibilities or speeds of sound, u, of these highly complex mixtures. This may be useful when applying other formalisms, as the Kirkwood–Buff integrals [20] where values of α_P

---

[*] Corresponding author. Tel.: +34 983 423757; fax: +34 983 423136.
E-mail address: jagl@termo.uva.es (J.A. González).

0040-6031/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2008.07.002

and κ_T are needed. As far as we know, the Flory model has been merely tested to predict α_P and κ_T of simple systems, as those involving two alkanes, or cyclohexane or benzene + n-alkane mixtures [21–23].

2. FLORY theory

In this section, we present a brief summary of the model. More details are given in the original works [13,14,24–26]. The Flory equation of state is given by:

$$\frac{\bar{P}\bar{V}}{\bar{T}} = \frac{\bar{V}^{1/3}}{\bar{V}^{1/3}-1} - \frac{1}{\bar{V}\bar{T}} \tag{1}$$

where $\bar{V} = V/V^*$; $\bar{P} = P/P^*$ and $\bar{T} = T/T^*$ are the reduced volume, pressure and temperature, respectively. Eq. (1) is valid for pure liquids and liquid mixtures. For pure liquids, the reduction parameters, V_i^*, P_i^* and T_i^* can be obtained from experimental data, such as the coefficients of thermal expansion,α_{Pi}, and the isothermal compressibility, κ_{Ti}. For mixtures, the corresponding parameters are calculated as follows:

$$V^* = x_1V_1^* + x_2V_2^* \tag{2}$$

$$T^* = \frac{\varphi_1P_1^* + \varphi_2P_2^* - \varphi_1\theta_2\chi_{12}}{\left((\varphi_1P_1^*/T_1^*) + (\varphi_2P_2^*/T_2^*)\right)} \tag{3}$$

$$P^* = \varphi_1P_1^* + \varphi_2P_2^* - \varphi_1\theta_2\chi_{12} \tag{4}$$

In Eqs. (3) and (4), $\varphi_i = x_iV_i^*/\sum x_iV_i^*$ is the segment fraction and $\theta_2 = \varphi_2/(\varphi_2 + S_{12}\varphi_1)$, the site fraction. S_{12} is the so-called geometrical parameter of the mixture, which, assuming that the molecules are spherical, is calculated as $S_{12} = (V_1^*/V_2^*)^{-1/3}$. The energetic parameter, χ_{12}, also present in Eqs. (3) and (4), is determined from

$$H^E = x_1P_1^*V_1^*\left(\frac{1}{\bar{V}_1} - \frac{1}{\bar{V}}\right) + x_2P_2^*V_2^*\left(\frac{1}{\bar{V}_2} - \frac{1}{\bar{V}}\right) + \frac{x_1V_1^*\theta_2\chi_{12}}{\bar{V}} \tag{5}$$

In this equation the reduced volume of the mixture, $\bar{V}$, is obtained from the equation of state. Therefore, the molar excess volume can be also calculated:

$$V^E = (x_1V_1^* + x_2V_2^*)(\bar{V} - \varphi_1\bar{V}_1 - \varphi_2\bar{V}_2) \tag{6}$$

From the equation of state, it is also possible to write expressions for the isobaric expansion coefficient and the isothermal compressibility of the mixture:

$$\alpha_P = \frac{1}{T^*}\frac{\bar{V}^{4/3}}{\bar{P}\bar{V}^2(\bar{V}^{1/3} - 2/3) + (4/3 - \bar{V}^{1/3})} \tag{7}$$

$$\kappa_T = \frac{1}{P^*\bar{T}}\left[\frac{1/3\bar{V}^{-2/3}}{(\bar{V}^{1/3}-1)^2} + \frac{1}{\bar{T}}\left(\bar{P} - \frac{1}{\bar{V}^2}\right)\right]^{-1} \tag{8}$$

at low pressures ($p \approx 0$), these expressions are reduced to the well-known equations [21,24]:

$$\alpha_P = \frac{1}{T^*}\frac{\bar{V}^{4/3}}{(4/3 - \bar{V}^{1/3})} \tag{9}$$

and

$$\kappa_T = \frac{3\bar{V}^2(\bar{V}^{1/3} - 1)}{P^*(4 - 3\bar{V}^{1/3})} \tag{10}$$

The adiabatic compressibility is calculated according to:

$$\kappa_S = \kappa_T - \frac{TV\alpha_P^2}{C_P} \tag{11}$$

where C_P is the molar isobaric heat capacity of the mixture, which is obtained from

$$C_P = C_V + \frac{TV\alpha_P^2}{\kappa_T} \tag{12}$$

In this expression, $C_V = x_1C_{V1} + x_2C_{V2}$, as in the Flory model, $C_V^E = 0$ [17]. Finally, the speed of sound is determined from the

Table 1

Physical constants of pure compounds at 298.15 K: V, molar volume; α_P, isobaric expansion coefficient; κ_S, adiabatic compressibility; κ_T, isothermal compressibility; C_P, isobaric heat capacity; C_V, isochoric heat capacity; u, speed of sound

Compound[a]	V (cm^3 mol^{-1})	α_P (10^{-3} K^{-1})	κ_S (TPa^{-1})	κ_T (TPa^{-1})	C_P (J mol^{-1} K^{-1})	C_V (J mol^{-1} K^{-1})	u (m s^{-1})
2ME	79.26[b]	0.956[b]	578.8[b]	704[b]	172.4[c]	141.7	1341.5[b]
2EE	97.43[b]	0.9833[b]	637.96[b]	773.5[b]	207.2[c]	170.9	1301.7[b]
2PE	114.75[d]	1.003[d]	652.4[d]	792[d]	246.5[d]	203.1	1299.6[d]
2BE	131.89[b]	0.9346[b]	655.33[b]	783[b]	268.9[c]	225.1	1305[b]
22MEE	118.31[e]	0.8767[e]	491.7[e]	595.2[e]	262.1[c]	216.6	1415.2[e]
22EEE	136.45[e]	0.9242[e]	538.4[e]	655.3[e]	297.2[c]	244.2	1374.3[e]
22BEE	171.11[e]	0.8918[e]	572.8[e]	687.1[e]	354.9[c]	295.8	1356.9[e]
Octane	163.58[d]	1.164[f]	1040.2[d]	1275.3[d]	254.2[d]	207.3	1173.3[d]
DBE	170.45[b]	1.1336[b]	971.2[b]	1205.9[b]	278.02[g]	224.04	1160.9[b]
MeOH	40.75[f]	1.196[f]	1028[f]	1248[f]	81.47[f]	67.1	1102[h]
EtOH	58.69[f]	1.096[f]	946[f]	1153[f]	112.34[f]	92.2	1143[h]
1-PrOH	75.16[f]	1.004[f]	849[f]	1026[f]	143.87[f]	119.1	1207.1[i]
1-BuOH	91.98[j]	0.9493[j]	808.1[j]	949.2[j]	171.1[c]	149.1	1239.2[j]
1-HpOH	141.90[k]	0.8599[k]	693.8[k]	808.7[k]	272.3[l]	233.6	1326.7[k]

[a] 2ME, 2-methoxyethanol; 2EE, 2-ethoxyethanol; 2PE, 2-propoxyethanol; 2BE, 2-butoxyethanol; 22MEE, 2-(2-methoxyethoxy)ethanol; 22EEE, 2-(2-ethoxyethoxy)ethanol; 22BEE, 2-(2-butoxyethoxy)ethanol; DBE, dibutylether; MeOH, methanol; EtOH, ethanol; 1-PrOH, 1-propanol; 1-BuOH, 1-butanol; 1-HpOH, 1-heptanol.

[b] [29].

[c] [52].

[d] [53].

[e] [30].

[f] [54].

[g] [55].

[h] [56].

[i] [57].

[j] [58].

[k] [59].

[l] [60].

Newton–Laplace equation [27]:

$$u = \frac{1}{(\rho \kappa_S)^{1/2}} \tag{13}$$

being ρ the density of the mixture.

3. Estimation of the Flory energetic parameter

In a previous paper [19], we have reported an expression to determine χ_{12} from a H^E measurement at a given composition:

$$\chi_{12} = \frac{x_1 P_1^* V_1^* (1 - (\bar{T}_1/\bar{T})) + x_2 P_2^* V_2^* (1 - (\bar{T}_2/\bar{T}))}{x_1 V_1^* \theta_2} \tag{14}$$

where $\bar{T}$ depends on H^E as follows:

$$H^E = \frac{x_1 P_1^* V_1^*}{\bar{V}_1} + \frac{x_2 P_2^* V_2^*}{\bar{V}_2} + \frac{1}{\bar{V}\bar{T}}(x_1 P_1^* V_1^* \bar{T}_1 + x_2 P_2^* V_2^* \bar{T}_2) \tag{15}$$

as $\bar{V}$ can be written as a $\bar{T}$ function taking into account the equation of state. For the sake of simplicity, we use here the so-called $\bar{p} \approx 0$ approximation of the equation of state ($\bar{T} = (\bar{V}^{1/3} - 1)/\bar{V}^{4/3}$) which is a good approximation at atmospheric pressure. Eq. (15) generalizes that which allows to obtain the χ_{12} parameter from H^E at equimolar composition [28].

The coefficients α_{Pi} and κ_{Ti} ($i = 1, 2$) of pure compounds, needed to calculate the corresponding reduction parameters, are listed in Table 1. The latter are collected in Table 2. Values of the χ_{12} parameter determined from H^E data at $x_1 = 0.5$ are given in Table 3. The concentration dependence of χ_{12} is shown for some selected mixtures in Fig. 1 Calculations were developed using Eq. (14) and smoothed H^E values at $\Delta x_1 = 0.05$ in the composition range [0.05, 0.95] (see below).

Table 2

Reduction parameters[a] for volume, V^*, and pressure, P^*, in the Flory model

Compound	V^* (cm^3 mol^{-1})	P^* (J cm^{-3})
2-Methoxyethanol	63.99	621.1
2-Ethoxyethanol	78.30	586.8
2-Propoxyethanol	91.92	588.4
2-Butoxyethanol	106.87	542.
2-(2-Methoxyethoxy)ethanol	96.83	655.6
2-(2-Ethoxyethoxy)ethanol	110.76	638.2
2-(2-Butoxyethoxy)ethanol	139.67	580.8
Octane	127.76	446.1
Dibutylether	133.74	455.4
Methanol	31.67	472.9
Ethanol	46.32	455
1-Propanol	60.19	454.8
1-Butanol	74.34	456.4
1-Heptanol	116.48	470.5

[a] Calculated using data collected in Table 1.

4. Results

Results on H^E and V^E obtained using χ_{12} values at $x_1 = 0.5$ are listed in Tables 4 and 5, respectively (Figs. 2 and 3). Tables 6 and 7 show the corresponding results for α_P, κ_S, κ_T and u (Figs. 4 and 5). For the sake of clarity, standard relative deviations defined as

$$\sigma_r(M) = \left[\frac{1}{N} \sum \left(\frac{M_{exp} - M_{calc}}{M_{exp}} \right)^2 \right]^{1/2} \tag{16}$$

are given for $M = H^E$ (Table 4); α_P, κ_S, κ_T (Table 6) and u (Table 7). In Eq. (16), N stands for the number of data points (=19, as all the experimental values used were obtained from smooth equations (essentially Redlich–Kister expansions) at $\Delta x_1 = 0.05$. The variation

Table 3

Molar excess functions, enthalpies, H^E, and internal energies at constant volume, U_V^E, at equimolar composition and 298.15 K

System[a]	H^E (J mol^{-1})	$X_{12}(H^E)$ (J cm^{-3})	U_V^E (J mol^{-1})	$X_{12}(U_V^E)$ (J cm^{-3})
2EE + octane	1126 [61]	47.57		
2PE + octane	1023 [61]	38.54		
2BE + octane	919 [61]	31.54		
2ME + DBE	1196 [62]	57.92	1098 [29]	53.20
2EE + DBE	1003 [62]	41.84	931 [29]	38.85
2BE + DBE	683 [63]	23.16	694 [29]	23.52
22MEE + DBE	1297 [62]	47.17	1244 [30]	45.27
22EEE + DBE	1117 [62]	36.84	1075 [30]	35.47
22BEE + DBE	819 [62]	23.41	854 [30]	24.39
2ME + 1-BuOH	695 [64]	39.85	632 [31]	36.24
2EE + 1-BuOH	442 [65]	22.13	419 [31]	20.98
2BE + 1-BuOH	301 [64]	12.36	321 [31]	13.19
22MEE + 1-BuOH	889 [64]	38.96	839[b]	36.77
22EEE + 1-BuOH	676 [64]	27.14	662[c]	26.58
22BEE + 1-BuOH	492 [64]	17.20	531[d]	18.56
2ME + 2EE	39 [66]	2.21	37[e]	2.09
2ME + 2BE	210 [66]	10.83	165[f]	8.51
2ME + 22MEE	−13.4 [66]	−0.629	−5.4[g]	−0.203
EtOH + octane	623 [67]	38.61		
1-PrOH + octane	646 [68]	33.05		
MeOH + DBE	800 [69]	66.41		
EtOH + DBE	858 [69]	52.66		
1-BuOH + DBE	840 [70]	36.5		
1-HpOH + DBE	772 [69]	25		

Also included are the energetic parameter, X_{12}, calculated from H^E and U_V^E at equimolar composition.

[a] For symbols, see Table 1.

[b] $A_0 = 3358.1$; $A_1 = -952$; $A_2 = 6$; $A_3 = 478$.

[c] $A_0 = 2646.9$; $A_1 = -947.9$.

[d] $A_0 = 2123.9$; $A_1 = 163.5$.

[e] $A_0 = 147.55$; $A_1 = -1.7$; $A_2 = 2.2$ $A_3 = 39.6$.

[f] $A_0 = 659.3$, 3358.1; $A_1 = 163.5$.

[g] $A_0 = -21.71$ $A_1 = -2$; $A_2 = -9.5$.

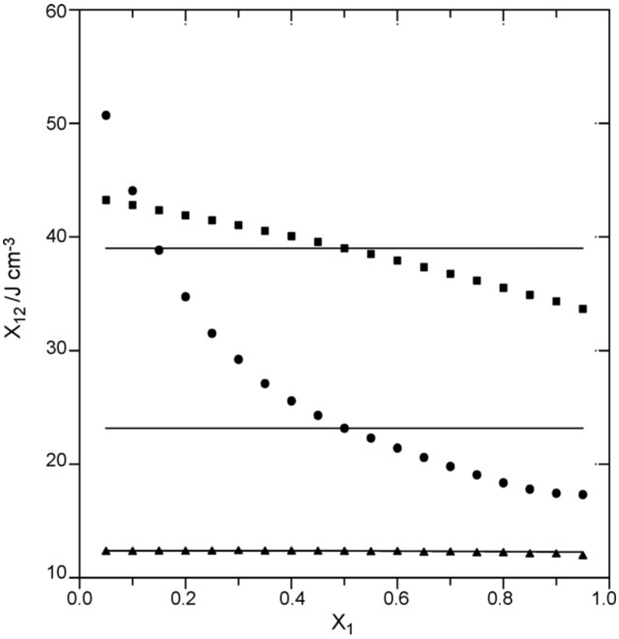

Fig. 1. χ_{12} parameter at 298.15 K for hydroxyether(1) + organic solvent(2) mixtures. Points, values obtained from H^E data: (●), 2-butoxyethanol + dibutylether [63]; (▲), 2-butoxyethanol + 1-butanol [64]; (■), 2-(2-methoxyethoxy)ethanol + 1-butanol [64]. Solid lines, χ_{12} values at x_1 = 0.5.

Table 4
Variations of the χ_{12} values, Δ_i, for hydroxyether + organic solvent mixtures in the concentration ranges [0.05, 0.5] (i = 1) and [0.5, 0.95] (i = 2) calculated according to Eq. (17)

System[a]	Δ_1	Δ_2	$\sigma_r(H^E)$[b]
2BE + octane	1.730	0.119	0.252
2BE + DBE	1.286	0.273	0.279
22MEE + DBE	0.683	0.072	0.169
2BE + 1-BuOH	0.004	0.031	0.013
22MEE + 1-BuOH	0.109	0.137	0.078
2ME + 2BE	0.083	0.083	0.250
1-HpOH + DBE	1.160	0.218	0.255

The standard relative deviations for HE, obtained using χ_{12} values listed in Table 3 are also given.

[a] For symbols, see Table 1; for the source of H^E experimental data, see Table 3.

[b] Eq. (16).

of χ_{12} with the concentration is estimated from the equation:

$$\Delta_i = 100\left|\frac{\chi_{12}^{\max,\min}(x_1) - \chi_{12}(x_1 = 0.5)}{\chi_{12}(x_1 = 0.5)}\right| \tag{17}$$

where $\chi_{12}^{\max}$ is the maximum absolute value of the χ_{12} in the range [0.05, 0.45] (i = 1) and $\chi_{12}^{\min}$ is the minimum absolute value in the range [0.55, 0.95] (i = 2). The corresponding values for a few systems are listed in Table 4.

5. Discussion

In some previous papers [29–31], we have determined the molar excess internal energy at constant volume, U_V^E, using the equation [32,33]:

$$U_V^E = H^E - \frac{T\alpha_P V^E}{\kappa_T} \tag{18}$$

for the systems 2-alkoxyethanol, or 2-(2-alkoxyethoxy)ethanol + dibutylether, and 2-alkoxyethanol + 1-butanol. U_V^E values, for 2-(2-alkoxyethoxy)ethanol + 1-butanol, and 2-methoxyethanol + alkoxyethanol mixtures, have been calculated in this work. Results of the corresponding Redlich–Kister expansions are given as footnotes in Table 3. We note that H^E and U_V^E values are rather close (Table 3), indicating that the contribution from the equation of state term to H^E is low, and that this excess function is mainly determined by interactional effects. As a consequence the α_P, κ_S, κ_T (Table 6) and u (Table 7) predictions obtained using χ_{12} from H^E or U_V^E data are rather similar (Tables 6 and 7). In the fol-

Table 5
Molar excess volumes, V^E, at equimolar composition and 298.15 K

System[a]	V^E (cm^3 mol^{-1})			Ref.
	Exp.	Calc. using $X_{12}(H^E)$	Calc. using $X_{12}(U_V^E)$	
2EE + octane	0.7535	0.616		[53]
2PE + octane	0.5882	0.533		[53]
2BE + octane	0.4445	0.372		[53]
2ME + DBE	0.3125	0.6348	0.5562	[29]
2EE + DBE	0.2260	0.5596	0.5018	[29]
2BE + DBE	−0.0544	0.2493	0.2537	[29]
22MEE + DBE	0.1582	0.2217	0.1842	[30]
22EEE + DBE	0.1417	0.2591	0.2292	[30]
22BEE + DBE	−0.1057	0.0462	0.0708	[30]
2ME + 1-BuOH	0.1869	0.4617	0.4195	[31]
2EE + 1-BuOH	0.0655	0.3283	0.3196	[31]
2BE + 1-BuOH	−0.0597	0.1882	0.2018	[31]
22MEE + 1-BuOH	0.1336	0.3911	0.3616	[58]
22EEE + 1-BuOH	0.0283	0.3642	0.3554	[58]
22BEE + 1-BuOH	−0.0967	0.2247	0.2488	[58]
2ME + 2EE	0.0066	0.0157	0.0146	[71]
2ME + 2BE	0.1252	0.1356	0.1087	[71]
2ME + 22MEE	−0.0187	−0.0315	−0.027	[71]
EtOH + octane	0.4931	0.5817		[72]
1-PrOH + octane	0.3641	0.5500		[72]
MeOH + DBE	−0.185	0.7500		[73]
EtOH + DBE	−0.150	0.789		[73]
1-BuOH + DBE	−0.239	0.678		[74]
1-HpOH + DBE	−0.368	0.4147		[59]

Comparison between experimental (exp.) data with theoretical results calculated using X_{12} values listed in Table 3.

[a] For symbols, see Table 1.

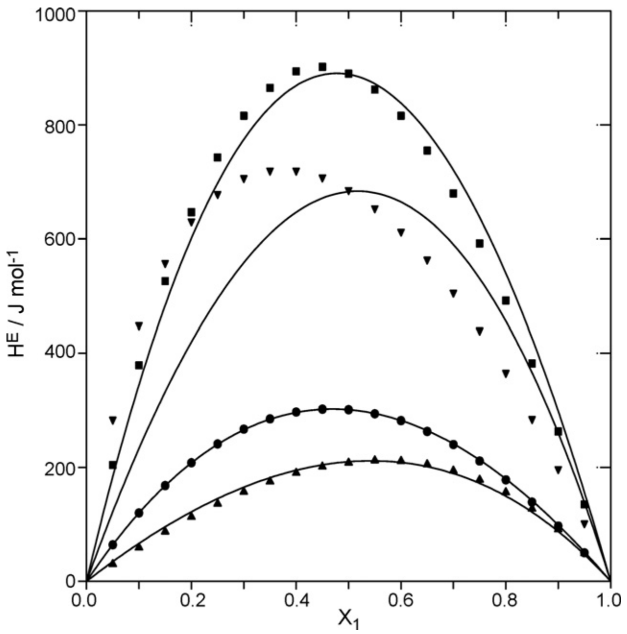

Fig. 2. H^E at 298.15 K for hydroxyether(1) + organic solvent(2) mixtures. Points, experimental results: (▲), 2-methoxyethanol + 2-butoxyethanol [66]; (●), 2-butoxyethanol + 1-butanol [64]; (▼), 2-butoxyethanol + dibutylether [63]; (■), 2-(2-methoxyethoxy)ethanol + 1-butanol [64]. Solid lines, Flory calculations.

Table 6

Standard relative deviations, σ_r, between experimental data for alkoxyethanol + organic solvent mixtures at 298.15 K and Flory calculations for isobaric expansion coefficient, α_P, adiabatic compressibility, κ_S, and isothermal compressibility, κ_T

System[a]	$\sigma_r(\alpha_P)$[b]		$\sigma_r(\kappa_S)$[b]		$\sigma_r(\kappa_T)$[b]	
	(A)[c]	(B)[d]	(A)[c]	(B)[d]	(A)[c]	(B)[d]
2EE + octane[e]			0.008		0.011	
2PE + octane[e]			0.007		0.006	
2BE + octane[e]			0.0185		0.025	
2ME + DBE[f]	0.005	0.005	0.010	0.008	0.015	0.010
2EE + DBE[f]	0.004	0.005	0.015	0.012	0.015	0.012
2BE + DBE[f]	0.005	0.005	0.014	0.012	0.011	0.012
22MEE + DBE[g]	0.002	0.002	0.009	0.011	0.007	0.008
22EEE + DBE[g]	0.002	0.003	0.005	0.007	0.003	0.004
22BEE + DBE[g]	0.002	0.002	0.001	0.002	0.003	0.004
2ME + 1-BuOH[h]	0.015	0.012	0.025	0.020	0.028	0.024
2EE + 1-BuOH[h]	0.011	0.010	0.020	0.018	0.021	0.020
2BE + 1-BuOH[h]	0.007	0.007	0.015	0.016	0.016	0.017
22MEE + 1-BuOH[i]	0.012	0.010	0.016	0.014	0.018	0.016
22EEE + 1-BuOH[i]	0.012	0.012	0.018	0.017	0.019	0.018
22BEE + 1-BuOH[i]	0.006	0.007	0.015	0.017	0.016	0.013
2ME + 2EE[j]	0.001	0.001	0.001	0.0009	0.0009	0.0008
2ME + 2BE[j]	0.005	0.004	0.0009	0.003	0.003	0.0008
2ME + 22MEE[j]	0.001	0.001	0.005	0.005	0.002	0.001
EtOH + octane[k]			0.005			
1-PrOH + octane[k]			0.012			
MeOH + DBE[l]			0.058			
EtOH + DBE[l]			0.055			
1-BuOH + DBE[m]	0.015		0.053			
1-HpOH + DBE[n]	0.014		0.034			

[a] For symbols, see Table 1.

[b] Eq. (16).

[c] Calculated using $X_{12}(H^E)$.

[d] Calculated using $X_{12}(U_V^E)$.

[e] [53].

[f] [29].

[g] [30].

[h] [31].

[i] [58].

[j] [71].

[k] [72].

[l] [75].

[m] [74].

[n] [59].

lowing, we will analyze the results obtained using χ_{12} values from H^E. It is known that the Flory model is typically applied to describe simultaneously H^E and V^E of systems formed by alkane and a polarizable component (benzene, cyclohexane) [34,35], or a slightly polar compound (ether, triethylamine) [36,37], or even to solutions containing two polar compounds of the same chemical nature (1-alkanol + 1-alkanol, 2-methoxyethanol + alkoxyethanol) [38,39]. Here, where very complex mixtures are considered, the model usually fails when representing H^E and V^E data. In the case of H^E, differences between experimental values and theoretical results depend on the orientational effects present in the mixtures under study. Large orientational effects lead to poor H^E results (Tables 3 and 4; [19]). For example, we note that orientational effects are stronger in 2-butoxyethanol + dibutylether than in 2-butoxyethanol + 1-butanol, which shows a nearly random mixing behavior (Fig. 1). Consequently, H^E is much better represented by the theory for the latter system (Fig. 2). However, structural effects are very important in this type of solutions [29–31] and V^E is poorly described (Table 5).

In order to investigate the influence of orientational effects on α_P, κ_S, κ_T and u predictions, let us consider the 2-butoxyethanol, 2-(2-methoxyethoxy)ethanol or 1-heptanol + dibutylether mixtures, as 2-butoxyethanol, 2-(2-methoxyethoxy)ethanol and 1-heptanol are isomeric molecules. The poor results obtained for the 1-heptanol system could be ascribed to the self-association of the alcohol. However, predictions are similar for the 2-butoxyethanol, 2-(2-methoxyethoxy)ethanol solutions, although orientational effects are much weaker in the latter mixture (Table 4), and even slightly poorer for the 2-butoxyethanol + 1-butanol system, characterized, as already mentioned, by random mixing. On the other hand, the better results are obtained for mixtures containing two hydroxyethers, where the theory provides a good representation for V^E (Fig. 5). It is then possible to conclude that α_P, κ_S, κ_T and u predictions mainly depend on the ability of the model to describe accurately structural effects. So, predictions on α_P, κ_S, κ_T and u can be improved using a χ_{12} parameter obtained from V^E data. A few examples follow. For the 2-methoxyethanol + 1-butanol system ($\chi_{12} = 16.1\ \mathrm{J\,cm^{-3}}$): $\sigma_r(\alpha_P) = 0.0008$; $\sigma_r(\kappa_S) = 0.001$; $\sigma_r(\kappa_T) = 0.002$; $\sigma_r(u) = 0.004$; for 2-(2-methoxyethoxy)ethanol + 1-butanol ($\chi_{12} = 19.6\ \mathrm{J\,cm^{-3}}$): $\sigma_r(\alpha_P) = 0.002$; $\sigma_r(\kappa_S) = 0.007$; $\sigma_r(\kappa_T) = 0.008$; $\sigma_r(u) = 0.008$; and for 1-butanol + dibutylether ($\chi_{12} = 1.5\ \mathrm{J\,cm^{-3}}$): $\sigma_r(\alpha_P) = 0.009$; $\sigma_r(\kappa_S) = 0.005$; $\sigma_r(u) = 0.001$.

Previously [31,40], we have used semiempirical equations for the u predictions of some hydroxyether + organic solvent mixtures. The equations applied were: free length theory (FLT) [41,42], collision factor theory (CFT) [43], and Nomoto [44], Junjie [45] and Van Dael [46] equations. A summary of the results is shown in Table 8. We note that the Van Dael equation provides the poorer results, which may be explained taking into account that this equation

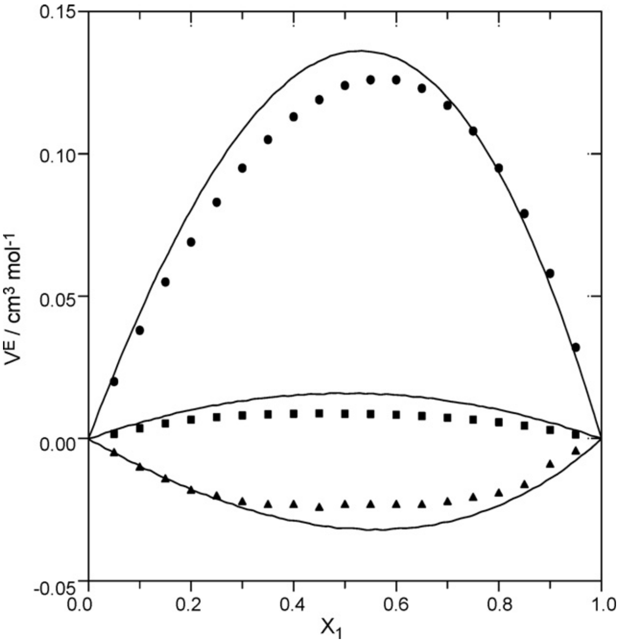

Fig. 3. V^E at 298.15 K for 2-methoxyethanol(1) + hydroxyether(2) mixtures. Points, experimental results [71]: (■), 2-ethoxyethanol; (●), 2-butoxyethanol; (▲), 2-(2-methoxyethoxy)ethanol. Solid lines, Flory calculations.

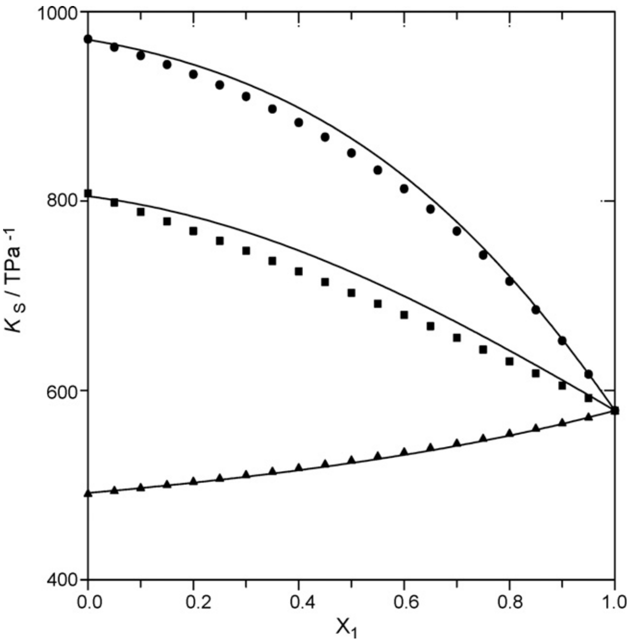

Fig. 5. κ_S at 298.15 K for 2-methoxyethanol(1) + hydroxyether(2) mixtures. Points, experimental results: (●), dibutylether [29]; (■), 1-butanol [31]; (▲), 2-(2-methoxyethoxy)ethanol [71]. Solid lines, Flory calculations.

is stated under the assumption $\kappa_S = x_1\kappa_{S1} + x_2\kappa_{S2}$. On the other hand, FLT yields a larger average $\sigma_r(u)$ value than those from CFT, Nomoto's or Junjie's equations (Table 8). This might be explained in terms of two important shortcomings of FLT: association and shape or size effects [47,48]. For example, it should be kept in mind that free length is calculated assuming that the molecules are spherical. The good results obtained from CFT, and from Nomoto's and Junjie's equations suggest that: (i) the available volume, for pure liquids and mixtures, is correctly calculated in the framework of the collision factor theory, (ii) the Rao's assumption on additivity of molar sound velocity contributions (Rao's constant) from atoms, atom groups and chemical bonds of the constituent molecules [49] is valid for this type of mixtures. In addition the Rao's constant varies linearly with the concentration for such solutions [31,40], and

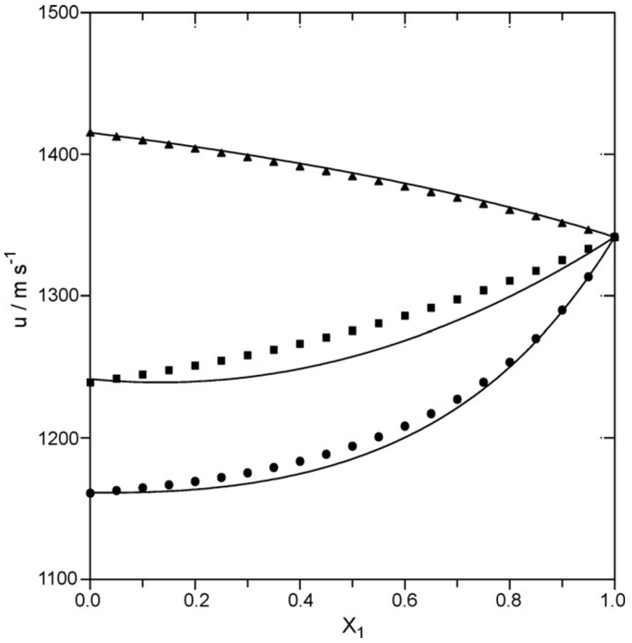

Fig. 4. u at 298.15 K for 2-methoxyethanol(1) + hydroxyether(2) mixtures. Points, experimental results: (●), dibutylether [29]; (■), 1-butanol [31]; (▲), 2-(2-methoxyethoxy)ethanol [71]. Solid lines, Flory calculations.

Table 7
Speeds of sound at equimolar composition and 298.15 K for alkoxyethanol + organic solvent mixtures

System[a]	u (m s^{-1})			$\sigma_r(u)$[b]		Ref.
	Exp.	(A)[c]	(B)[d]	(A)[c]	(B)[d]	
2EE + n-C$_8$	1186.3	1196.6		0.021		[53]
2PE + n-C$_8$	1197.9	1206.3		0.020		[53]
2BE + n-C$_8$	1208.9	1215.1		0.015		[53]
2ME + DBE	1194.1	1185.1	1188.6	0.012	0.007	[29]
2EE + DBE	1195.8	1185.	1187.4	0.015	0.011	[29]
2BE + DBE	1215.9	1207.7	1207.4	0.011	0.012	[29]
22MEE + DBE	1233.6	1243.3	1244.9	0.013	0.016	[30]
22EEE + DBE	1232.3	1237.8	1239.2	0.005	0.009	[30]
22BEE + DBE	1245.5	1246.5	1245.6	0.002	0.002	[30]
2ME + 1-BuOH	1284.4	1257.3	1259	0.023	0.019	[31]
2EE + 1-BuOH	1276.5	1254	1253.7	0.017	0.016	[31]
2BE + 1-BuOH	1270.3	1268.8	1266.8	0.013	0.014	[31]
22MEE + 1-BuOH	1326.1	1314.8	1316.8	0.015	0.012	[58]
22EEE + 1-BuOH	1314.2	1303	1303.6	0.015	0.014	[58]
22BEE + 1-BuOH	1315.6	1305	1303.7	0.014	0.016	[58]
2ME + 2EE	1318.8	1318.2	1318.3	0.0006	0.0005	[71]
2ME + 2BE	1312.2	1311.2	1313	0.001	0.001	[71]
2ME + 22MEE	1384.5	1386.8	1386.5	0.003	0.002	[71]
EtOH + octane	1144.7	1146.9		0.018		[72]
1-PrOH + octane	1165.4	1154.3		0.019		[72]
MeOH + DBE	1144.8	1113.4		0.055		[75]
EtOH + DBE	1152.4	1041.9		0.052		[75]
1-BuOH + DBE	1187.3	1156.9		0.045		[74]
1-HpOH + DBE	1233.2	1210.7		0.031		[59]

Comparison between experimental data and calculated results from the Flory model Standard relative deviations, $\sigma_r(u)$ are also included.

[a] For symbols, see Table 1.

[b] Eq. (16).

[c] Calculated using $X_{12}(H^E)$.

[d] Calculated using $X_{12}(U_V^E)$.

Table 8
Mean standard relative deviations[a] for speeds of sound for alkoxythanol + organic solvent mixtures calculated according to different models

System	Flory	FLT	CFT	Nomoto	Junjie	Van Dael
2-Alkoxyethanol + n-C_8	0.019	0.005[b]	0.015[b]	0.018[b]	0.005[b]	0.021[b]
2-Alkoxyethanol + DBE	0.013	0.013[b]	0.009[b]	0.007[b]	0.002[b]	0.013[b]
2-(2-Alkoxyethoxy)ethanol + DBE	0.007	0.013[b]	0.013[b]	0.011[b]	0.008[b]	0.015[b]
2-Alkoxyethanol + 1-butanol	0.018	0.032[c]	0.003[c]	0.003[c]	0.004[c]	0.035[c]
2-(2-Alkoxyethoxy)ethanol + 1-butanol	0.015	0.024[c]	0.003[c]	0.004[c]	0.007[c]	0.052[c]

[a] Calculated as $\frac{1}{N}\sum \sigma_r(u)$ where N (=3) is the number of mixtures for each group of systems (see Table 7).

[b] [40].

[c] [31].

this indicates the absence of complex formation [50,51]. (iii) The compressibility of these systems may be estimated by the simple equation: $\kappa_S = \phi_1\kappa_{S1} + \phi_2\kappa_{S2}$; the larger deviations obtained from Flory theory are due to calculations are developed on χ_{12} parameters estimated from H^E data. In contrast, $\sigma_r(u)$ values obtained using χ_{12} parameters calculated on the basis of V^E data compare well with those provided by CFT, or Nomoto's or Junjie's equations (see above).

6. Conclusions

Deviations between experimental isobaric expansion coefficients, isentropic or isothermal compressibilities and speeds of sound data and calculated values in the framework of the Flory theory depend on the ability of the model to represent structural effects present in the complex mixtures studied. Better predictions are obtained when χ_{12} is obtained from V^E data.

Acknowledgements

The authors gratefully acknowledge the financial support received from the Consejería de Educación y Cultura of Junta de Castilla y León, under Projects VA080A06 and VA075A07 and from the Ministerio de Educación y Ciencia, under the Project FIS2007-61833.

References

[1] A. Heintz, R.N. Lichtenthaler, Ber. Bunsenges. Phys. Chem. 81 (1977) 921–925.
[2] T.M. Letcher, W.C. Spiteri, J. Chem. Thermodyn. 11 (1979) 435–440.
[3] S.N. Battacharyya, D. Patterson, J. Phys. Chem. 83 (1979) 2979–2985.
[4] T.M. Letcher, J. Chem. Thermodyn. 16 (1984) 805–810.
[5] T.M. Letcher, D.M. Perkins, Thermochim. Acta 77 (1984) 267–274.
[6] G. Tardajos, E. Aicart, M. Costas, D. Patterson, J. Chem. Soc., Faraday Trans. 1 82 (1986) 2977–2987.
[7] A.D. Mantilla, G. Tardajos, E. Junquera, E. Aicart, J. Solution Chem. 20 (1991) 805–816.
[8] S.N. Battacharyya, M. Costas, D. Patterson, H.-V. Tra, Fluid Phase Equilib. 20 (1985) 27–45.
[9] D. Patterson, J. Solution Chem. 23 (1994) 105–120.
[10] M. Costas, D. Patterson, Thermochim. Acta 120 (1987) 161–181.
[11] E. Wilhelm, A. Laínez, A.H. Roux, J.-P.E. Grolier, Thermochim. Acta 105 (1986) 101–110.
[12] M. Costas, H. Van Tra, D. Patterson, M. Cáceres, G. Tardajos, E. Aicart, J. Chem. Soc., Faraday Trans. I 84 (1988) 1603–1616.
[13] P.J. Flory, J. Am. Chem. Soc. 87 (1965) 1833–1838.
[14] A. Abe, P.J. Flory, J. Am. Chem. Soc. 87 (1965) 1838–1846.
[15] H.T. Van, D. Patterson, J. Solution Chem. 11 (1982) 793–805.
[16] E. Aicart, G. Tardajos, M. Costas, J. Solution Chem. 18 (1989) 369–377.
[17] A. Domínguez, G. Tardajos, E. Aicart, S. Pérez-Casas, L.M. Trejo, M. Costas, D. Patterson, H.V. Tra, J. Chem. Soc., Faraday Trans. 89 (1993) 89–93.
[18] D. Patterson, Thermochim. Acta 267 (1995) 15–27.
[19] J.A. González, N. Riesco, I. Mozo, I. García de la Fuente, J.C. Cobos, Ind. Eng. Chem. Res. 46 (2007) 1350–1359.
[20] (a) A. Ben-Naim, J. Chem. Phys. 67 (1977) 4884–4890;
(b) J. Zielkiewicz, Phys. Chem. Chem. Phys. 2 (2000) 2925–2932.
[21] G.C. Benson, C.J. Halpin, Can. J. Chem. 65 (1987) 322–325.
[22] E. Aicart, C. Menduiña, R.L. Arenosa, G. Tardajos, J. Solution Chem. 13 (1984) 443–455.
[23] E. Aicart, C. Menduiña, R.L. Arenosa, G. Tardajos, J. Solution Chem. 12 (1983) 703–716.
[24] P.J. Flory, R.A. Orwoll, A. Vrij, J. Am. Chem. Soc. 86 (1964) 3507–3514.
[25] P.J. Flory, R.A. Orwoll, A. Vrij, J. Am. Chem. Soc. 86 (1964) 3515–3520.
[26] R.A. Orwoll, P.J. Flory, J. Am. Chem. Soc. 89 (1967) 6822.
[27] O. Kiyohara, C.J. Halpin, G.C. Benson, J. Chem. Thermodyn. 10 (1978) 721–730.
[28] P.J. Howell, B.J. Skilleme de Bristowe, D. Stubley, J. Chem. Soc. A (1971) 397–400.
[29] I. Mozo, I. García de la Fuente, J.A. González, J.C. Cobos, J. Mol. Liq. 129 (2006) 155–163.
[30] I. Mozo, I. García de la Fuente, J.A. González, J.C. Cobos, J. Mol. Liq. 136 (2007) 117–127.
[31] I. Mozo, J.A. González, I. García de la Fuente, J.C. Cobos, N. Riesco, J. Mol. Liq. 140 (2008) 87–100.
[32] J.S. Rowlinson, F.L. Swinton, Liquids and Liquid Mixtures, third ed., Butterworths, London, 1982.
[33] H. Kalali, F. Kohler,. Svejda, Fluid Phase Equilibr. 20 (1985) 75–80.
[34] T.M. Letcher, R.C. Baxter, J. Solution Chem. 18 (1989) 65–79.
[35] A.M. Awwad, A.M. Salman, Fluid Phase Equilib. 25 (1986) 195–208.
[36] N. Riesco, J.A. González, S. Villa, I. García de la Fuente, J.C. Cobos, Phys. Chem. Liq. 41 (2003) 309–321.
[37] L. Wang, G.C. Benson, B.C.-Y. Lu, Thermochim. Acta 213 (1993) 83–103.
[38] G.C. Benson, H.D. Pflug, J. Chem. Eng. Data 15 (1970) 382–386.
[39] N. Riesco, S. Villa, J.A. González, I. García de la Fuente, J.C. Cobos, Thermochim. Acta 362 (2000) 89–97.
[40] J.A. González, I. Mozo, I. García de la Fuente, J.C. Cobos, N. Riesco, Phys. Chem. Liq. 46 (2008) 390–407.
[41] B. Jacobson, Acta Chem. Scand. A 6 (1952) 1485–1498.
[42] B. Jacobson, J. Chem. Phys. 20 (1952) 927–928.
[43] W. Schaaffs, Acustica 33 (1975) 272–276.
[44] O. Nomoto, J. Phys. Chem. 21 (1953) 950–951.
[45] Z. Junjie, J. China Univ. Sci. Techn. 14 (1984) 298.
[46] W. Van Dael, Themodynamic Properties and Velocity of Sound, Butterworths, 1975.
[47] V.A. Tabhane, S. Agarwal, M. Kalidoss, Phys. Chem. Liq. 40 (2002) 39–45.
[48] A. Ali, K. Nain, Pramana J. Phys. 58 (2002) 695–701.
[49] J. Glinski, J. Solution Chem. 31 (2002) 59–70.
[50] O. Nomoto, J. Phys. Chem. Jpn. 13 (1958) 1524–1528.
[51] R. Abraham, R.A. Abdulkhadar, C.V. Asokan, J. Chem. Thermodyn. 32 (2000) 1–16.
[52] J.C. Cobos, Ph.D. Thesis. Valladolid (1987).
[53] K. Tamura, A. Osaki, S. Murakami, B. Laurent, J.-P.E. Grolier, Fluid Phase Equilib. 173 (2000) 285–296.
[54] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents, fourth ed., Wiley, New York, 1986.
[55] J.C. Cobos, C. Casanova, G. Roux-Desgranges, J.-P.E. Grolier, J. Chem. Thermodyn. 19 (1987) 791–796.
[56] J. Canosa, A. Rodríguez, J. Tojo, Fluid Phase Equilib. 156 (1999) 57–71.
[57] C. González, M. Iglesias, J. Lanz, G. Marino, B. Orge, J.M. Resa, J. Eng. Food 50 (2001) 29–40.
[58] I. Mozo, I. García de la Fuente, J.A. González, J.C. Cobos, J. Chem. Eng. Data 52 (2007) 2086–2090.
[59] J.A. González, I. Mozo, I. García de la Fuente, J.C. Cobos, N. Riesco, J. Chem. Thermodyn. 40 (2008) 1495–1508.
[60] L. Andreolli-Ball, D. Patterson, M. Costas, M. Cáceres-Alonso, J. Chem. Soc. Faraday Trans. 1 84 (1988) 3991–4012.
[61] K. Tamura, A. Osaki, S. Murakami, H. Ohji, H. Ogawa, B. Laurent, J.-P.E. Grolier, Fluid Phase Equilib. 156 (1999) 137–147.
[62] J.C. Cobos, C. Casanova, J. Chem. Thermodyn. 19 (1987) 751–755.
[63] M.A. Villamañán, C. Casanova, A.H. Roux, J.-P.E. Grolier, J. Chem. Eng. Data 27 (1982) 89–91.
[64] J.C. Cobos, C. Casanova, Fluid Phase Equilib. 20 (1985) 155–160.
[65] M. Pintos, R. Bravo, M.I. Paz Andrade, V. Pérez Villar, J. Chem. Thermodyn. 14 (1982) 951–955.
[66] J.C. Cobos, I. García, C. Casanova, G. Roux-Desgranges, J.-P.E. Grolier, Thermochim. Acta 137 (1989) 241–246.
[67] V. Ragaini, R. Santi, S. Carrá, Lincei-Rend. Sc. Mat e Nat. 45 (1968) 540–549.

[68] E. Jiménez, C. Franjo, L. Segade, J.L. Legido, M.I. Paz Andrade, Fluid Phase Equilib. 133 (1997) 179–185.
[69] M.A. Villamañán, C. Casanova, A.H. Roux, J.P.E. Grolier, J. Chem. Thermodyn. 14 (1982) 251–258.
[70] K. Kammerer, R.N. Lichtenthaler, Thermochim. Acta 310 (1998) 61–67.
[71] I. Mozo, I. García de la Fuente, J.A. González, J.C. Cobos, N. Riesco, J. Chem. Eng. Data 53 (2008) 1404–1410.
[72] B. Orge, M. Iglesias, A. Rodrígiez, J.M. Canosa, J. Tojo, Fluid Phase Equilib. 133 (1997) 213–227.
[73] E.N. Rezanova, K. Kammerer, R.N. Lichtenthaler, J. Chem. Eng. Data 44 (1999) 1235–1239.
[74] I. Mozo, I. García de la Fuente, J.A. González, J.C. Cobos, J. Chem. Eng. Data 53 (2008) 857–862.
[75] A. Arce, E. Rodil, A. Soto, J. Solution Chem. 27 (1998) 911–923.