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Application of the Prigogine–Flory–Patterson model to excess volumes of mixtures of tetrahydrofuran or tetrahydropyran with cyclohexane or toluene

P. Brocos, A. Amigo, M. Pintos, E. Calvo, R. Bravo *

Departamento de Física Aplicada, Facultad de Física, Universidad de Santiago, E-15706, Santiago de Compostela, Spain

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Abstract

Excess molar volumes V_m^E at the temperatures 288.15 K, 298.15 K and 308.15 K and normal atmospheric pressure of binary mixtures of tetrahydrofuran or tetrahydropyran with cyclohexane or toluene have been computed from density measurements. From the results, the thermal expansion coefficients, α, were estimated. The Prigogine–Flory–Patterson theory and its applicability in predicting V_m^E is tested.

Keywords: Molar volumes; Prigogine-Flory-Patterson model; Thermal expansion coefficients; Prediction

1. Introduction

During recent years our primary aim has been the study of the main thermodynamic properties of mixtures of non-electrolytes, with special stress in those mixtures containing cyclic ethers, alkanols, and hydrocarbons [1–6]. In this work following the same programme we have determined the excess molar volumes V_m^E of binary systems $[x\text{c-}(CH_2)_pO + (1-x)\{\text{c-}C_6H_{12} \text{ or } C_6H_5CH_3\}]$ ($p = 4, 5$; c = cyclo), at the temperatures 288.15 K, 298.15K, 308.15 K and normal atmospheric pressure.

The scope of this work is to analyze the variations of the excess volumes under isobaric temperature changes, the influence of the hydrocarbon chain length of the ether upon V_m^E and the significance of the aromatic ring of the hydrocarbon.

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* Corresponding author.

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We have also performed a theoretical study under the frame work of the Prigogine–Flory–Patterson (PFP) molecular model [7–9]. This model, born as a modification of Flory's theory [10,11], has been successfully applied to a large variety of liquid mixtures. Nevertheless, the theoretical basis of the model gives rise to some restrictions in its application, for instance, hydrogen bonds, strong dipolar interactions, complex formation,... are excluded from this model. The origin of these limitations lies in the proper definition of the only adjustable parameter of the theory, χ_{12}, which derives from the contribution of two factors: on the one hand the relative weakness of the interaction between unlike molecules compared with those between like molecules, and, on the other, the difference in the diameters of the mixture components. The first factor reduces the field of application of this theory to those solutions where the intermolecular forces between unlike molecules are smaller than those interactions present in pure liquids. In this work we will analyze the influence of these limitations on the prediction of excess volumes with the PFP model. To evaluate this effect we have applied this model to the mixtures under study and we have compared the predicted V_m^E with our experimental values.

2. Experimental

The liquids used: tetrahydrofuran (THF), puriss. p.a., >0.995; tetrahydropyran (THP), purum, >0.99; cyclohexane, puriss. p.a., >0.995 and toluene, puriss. p.a., >0.995, were obtained from Fluka and subjected to no further purification. All the chemicals, except cyclohexane, were stored over molecular sieves (Union Carbide 0.4 nm, from Fluka).

The solutions for the measurements of densities were prepared by mass using a Mettler AT201 balance (precision 10^{-5} g), and air-tight stoppered bottles. The possible error in the mole fraction is estimated to be less than 10^{-4}.

Densities of pure components and their mixtures were measured with an Anton Paar (model DMA 60/602) densimeter operated in the static mode and capable of a precision of better than 10^{-5} g cm^{-3}. Table 1 reports the densities of the pure liquids at the temperatures 288.15 K, 298.15 K and 308.15 K together with the corresponding literature values, [1,2,5,6,12–19].

The temperature of the densimeter cell was controlled by an Anton Paar DT100 thermometer, and maintained constant to within 0.01 K using a Heto (type 04 PT 623) circulating thermostat. Bidistilled and deionized water [20] and dry air [21] were used as calibrating substances.

3. Results and discussion

Table 2 shows the experimental excess molar volumes at the temperatures 288.15 K, 298.15 K and 308.15 K. Each set of results was fitted to Eq. (1) [22]:

$$V_m^E/(\mathrm{cm^3\,mol^{-1}}) = x(1-x)\sum_{i=1}^{N} A_i(2x-1)^{i-1} \qquad (1)$$

Table 1
Experimental densities, ρ, of pure components at the temperatures 288.15 K, 298.15 K and 308.15 K

Compound	T/K	ρ/(g cm^{-3})	
		Experimental	Literature
c-$(CH_2)_4O$	28815	0.89286	
	298.15	0.88196	0.882339 [12], 0.882698 [13] 0.88195 [2], 0.88197 [14]
	308.15	0.87104	0.8712 [15]
c-$(CH_2)_5O$	288.15	0.88890	0.88892 [6]
	298.15	0.87885	0.87905 [16], 0.879103 [1] 0.87886 [1], 0.87891 [5]
	308.15	0.86881	0.86882 [5], 0.86880 [6]
c-C_6H_{12}	288.15	0.78311	
	298.15	0.77368	0.77368 [16], 0.7737 [17]
	308.15	0.76424	
$C_6H_5CH_3$	288.15	0.87144	
	298.15	0.86215	0.862149 [12], 0.86219 [18]
	308.15	0.85290	0.85286 [19], 0.8522 [15]

using a linear (unweighted) least-square fitting procedure. In each case, the optimum number of coefficients was determined using an F-test [23]. Table 3 reports the values of the parameters A_i together with the standard deviations of each fit.

We have compared our experimental values of V_m^E with those found in the literature, [12,15–17,24,25]; in Table 4 we report the discrepancies at equimolar concentrations.

In order to obtain the thermal expansion coefficients of the pure liquids, the experimental values of densities of each system have been fitted to a polynomial function:

$$\rho/(\mathrm{g\,cm^{-3}}) = \sum_{i=1}^{N} \sum_{j=1}^{3} A_{ij}(T-T_0)^{j-1}x^{i-1} \tag{2}$$

The thermal expansion coefficients α are therefore obtained by using the equation:

$$\alpha/\mathrm{kK^{-1}} = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \tag{3}$$

Table 5 lists the calculated values of α for the pure liquids at the temperatures 288.15 K, 298.15 K and 308.15 K, together with those found in the literature [26–29]; the agreement between our results and the literature data is quite good.

For the analyzed mixtures we can see that the excess molar volumes increase slightly with temperature and that the V_m^E–x curves are almost symmetrical about $x = 0.5$.

All the excess volumes for {THF or THP + cyclohexane} mixtures are positive, whereas for the binary mixtures containing toluene all the values are negative as

Table 2
Experimental excess molar volumes V_m^E at the temperature T

x	$V_m^E/cm^3\ mol^{-1}$	x	$V_m^E/cm^3\ mol^{-1}$	x	$V_m^E/cm^3\ mol^{-1}$	x	$V_m^E/cm^3\ mol^{-1}$
T = 288.15 K							
xc-$(CH_2)_4O$ + $(1-x)$c-C_6H_{12}							
0.0556	0.1333	0.3570	0.5079	0.6460	0.4657	0.9478	0.1115
0.1238	0.2684	0.4275	0.5288	0.7232	0.4074		
0.2163	0.3993	0.5028	0.5315	0.7987	0.3262		
0.2765	0.4549	0.5746	0.5135	0.8658	0.2430		
xc-$(CH_2)_5O$ + $(1-x)$c-C_6H_{12}							
0.0573	0.0849	0.3528	0.2921	0.6482	0.2716	0.9470	0.0625
0.1372	0.1661	0.4244	0.3068	0.7133	0.2398		
0.2042	0.2206	0.4993	0.3083	0.7910	0.1960		
0.2745	0.2609	0.5729	0.2946	0.8660	0.1366		
xc-$(CH_2)_4O$ + $(1-x)C_6H_5CH_3$							
0.0518	−0.0751	0.3494	−0.3331	0.6490	−0.3454	0.9417	−0.0818
0.1250	−0.1553	0.4207	−0.3582	0.7138	−0.3132		
0.2057	−0.2365	0.4956	−0.3702	0.7893	−0.2537		
0.2749	−0.2906	0.5680	−0.3656	0.8648	−0.1776		
xc-$(CH_2)_5O$ + $(1-x)C_6H_5CH_3$							
0.0525	−0.0302	0.3509	−0.1486	0.6426	−0.1535	0.9440	−0.0381
0.1258	−0.0717	0.4198	−0.1563	0.7138	−0.1378		
0.1529	−0.0844	0.4972	−0.1636	0.7912	−0.1173		
0.2743	−0.1295	0.5649	−0.1605	0.8700	−0.0755		
T = 298.15 K							
xc-$(CH_2)_4O$ + $(1-x)$c − C_6H_{12}							
0.0530	0.1198	0.3537	0.5079	0.6499	0.4748	0.9471	0.1191
0.1287	0.2657	0.4248	0.5379	0.7217	0.4138		
0.2089	0.3870	0.5053	0.5362	0.7985	0.3300		
0.2805	0.4604	0.5731	0.5126	0.8669	0.2349		

xc-$(CH_2)_5O + (1-x)$c-C_6H_{12}							
0.0601	0.0863	0.3385	0.2943	0.6480	0.2708	0.9029	0.0973
0.1344	0.1675	0.4203	0.3066	0.7203	0.2407		
0.2060	0.2234	0.4987	0.3089	0.7933	0.1906		
0.2792	0.2687	0.5725	0.2957	0.8642	0.1296		
xc-$(CH_2)_4O + (1-x)C_6H_5CH_3$							
0.0564	−0.0737	0.3543	−0.3232	0.6484	−0.3462	0.9482	−0.0831
0.1276	−0.1572	0.4278	−0.3544	0.7238	−0.3099		
0.2048	−0.2270	0.4963	−0.3691	0.7963	−0.2537		
0.2803	−0.2890	0.5696	−0.3692	0.8729	−0.1726		
xc-$(CH_2)_5O + (1-x)C_6H_5CH_3$							
0.0607	−0.0376	0.3513	−0.1462	0.6433	−0.1532	0.9430	−0.0408
0.1317	−0.0754	0.4246	−0.1572	0.7154	−0.1364		
0.2098	−0.1093	0.4993	−0.1619	0.7986	−0.1092		
0.2734	−0.1260	0.5900	−0.1600	0.8691	−0.0788		
$T = 308.15$ K							
xc-$(CH_2)_4O + (1$-$x)$c-C_6H_{12}							
0.0590	0.1401	0.3567	0.5175	0.6449	0.4962	0.9451	0.1440
0.1273	0.2746	0.4267	0.5477	0.7250	0.4244		
0.2080	0.3928	0.5011	0.5548	0.7989	0.3400		
0.2807	0.4685	0.5727	0.5292	0.8664	0.2484		
xc-$(CH_2)_5O + (1-x)$c-C_6H_{12}							
0.0567	0.0813	0.3556	0.3087	0.6499	0.2837	0.9541	0.0598
0.1303	0.1654	0.4184	0.3196	0.7213	0.2473		
0.2060	0.2323	0.5023	0.3217	0.7924	0.1956		
0.2780	0.2793	0.5739	0.3078	0.8696	0.1382		
xc-$(CH_2)_4O + (1-x)C_6H_5CH_3$							
0.0586	−0.0737	0.3562	−0.3318	0.6501	−0.3419	0.9452	−0.0837
0.1286	−0.1529	0.4289	−0.3561	0.7201	−0.3070		
0.2068	−0.2311	0.5019	−0.3696	0.7960	−0.2537		
0.2769	−0.2857	0.5773	−0.3625	0.8656	−0.1825		
xc-$(CH_2)_5O + (1-x)C_6H_5CH_3$							
0.0573	−0.0290	0.3533	−0.1431	0.6479	−0.1428	0.9462	−0.0337
0.1336	−0.0685	0.4262	−0.1507	0.7176	−0.1289		
0.2072	−0.1005	0.5009	−0.1556	0.7896	−0.1078		
0.2734	−0.1231	0.5722	−0.1537	0.8727	−0.0676		

Table 3
Parameters, A_i, and standard deviations, s, for least- squares fits of Eq. (1)

System	A_1	A_2	A_3	A_4	s
$T = 288.15$ K					
$x\text{c-(CH}_2)_4\text{O} + (1-x)\text{c-C}_6\text{H}_{12}$	2.1144	−0.2659	0.2711	–	0.0041
$x\text{c-(CH}_2)_5\text{O} + (1-x)\text{c-C}_6\text{H}_{12}$	1.2237	−0.1543	0.1411	–	0.0024
$x\text{c-(CH}_2)_4\text{O} + (1-x)\text{C}_6\text{H}_5\text{CH}_3$	−1.4863	−0.0683	–	–	0.0024
$x\text{c-(CH}_2)_5\text{O} + (1-x)\text{C}_6\text{H}_5\text{CH}_3$	−0.6591	−0.0336	–	–	0.0024
$T = 298.15$ K					
$x\text{c-(CH}_2)_4\text{O} + (1-x)\text{c-C}_6\text{H}_{12}$	2.1425	−0.2307	0.1602	–	0.0059
$x\text{c-(CH}_2)_5\text{O} + (1-x)\text{c-C}_6\text{H}_{12}$	1.2363	−0.1543	0.0886	−0.1126	0.0024
$x\text{c-(CH}_2)_4\text{O} + (1-x)\text{C}_6\text{H}_5\text{CH}_3$	−1.4782	−0.1397	–	–	0.0031
$x\text{c-(CH}_2)_5\text{O} + (1-x)\text{C}_6\text{H}_5\text{CH}_3$	−0.6484	−0.0322	−0.0545	–	0.0014
$T = 308.15$ K					
$x\text{c-(CH}_2)_4\text{O} + (1-x)\text{c-C}_6\text{H}_{12}$	2.1920	−0.1906	0.2521	–	0.0101
$x\text{c-(CH}_2)_5\text{O} + (1-x)\text{c-C}_6\text{H}_{12}$	1.2849	−0.1755	0.1047	–	0.0028
$x\text{c-(CH}_2)_4\text{O} + (1-x)\text{C}_6\text{H}_5\text{CH}_3$	−1.4744	−0.1228	–	–	0.0017
$x\text{c-(CH}_2)_5\text{O} + (1-x)\text{C}_6\text{H}_5\text{CH}_3$	−0.6236	−0.0228	–	–	0.0020

Table 4
Comparison of our V_m^E ($x = 0.5$) with literature values

System	T/K	Ref.	Discrepancy/ %
$x\text{c-(CH}_2)_4\text{O} + (1-x)\text{c-C}_6\text{H}_{12}$	298.15	Meyer et al. (1975) [24]	0.93
		Arm and Bankay (1969) [17]	4.6
$x\text{c-(CH}_2)_5\text{O} + (1-x)\text{c-C}_6\text{H}_{12}$	298.15	Inglese et al. (1984) [16]	2.5
$x\text{c-(CH}_2)_4\text{O} + (1-x)\text{C}_6\text{H}_5\text{CH}_3$	298.15	Francesconi and Comelli (1992) [12]	0.64
		Mahl et al. (1978) [25]	7.0
	308.15	Oswal et al. (1979) [15]	0.69
$x\text{c-(CH}_2)_5\text{O} + (1-x)\text{C}_6\text{H}_5\text{CH}_3$	298.15	Francesconi and Comelli (1992) [12]	1.7

indicated in Figs. 1(a) and (b). These figures also show that V_m^E in mixtures with THF is bigger than in those mixtures with THP.

The positive excess volumes in mixtures with cyclohexane can be understood in terms of the breaking of the dipole–dipole interaction between ether molecules. In mixtures with toluene the strong interaction between the π electron clouds and the ether dipoles is dominant compared with the breaking of dipole–dipole interactions; this results in complex formation and therefore negative excess volumes.

The fact that mixtures with THF produce greater excess volumes than those with THP is due to the greater polarity of THF [29]. The influence is stressed in mixtures with cyclohexane because of the steric effects due to the similar conformations of cyclohexane and tetrahydropyran.

Table 5
Thermal expansion coefficients, α, of pure liquids calculated from Eqs. (2) and (3)

Compound	T/K	α/kK^{-1}	
		Experimental	Literature
c-$(CH_2)_4O$	288.15	1.205	
	298.15	1.242	
	308.15	1.279	
c-$(CH_2)_5O$	288.15	1.120	
	298.15	1.144	
	308.15	1.168	
c-C_6H_{12}	288.15	1.186	1.188 [26]
	298.15	1.216	1.213 [26], 1.217 [28], 1.220 [29]
	308.15	1.247	1.241 [26]
$C_6H_5CH_3$	288.15	1.063	1.070 [26], 1.053 [27]
	298.15	1.080	1.087 [26], 1.078 [27], 1.067 [29]
	308.15	1.097	1.106 [26], 1.104 [27]

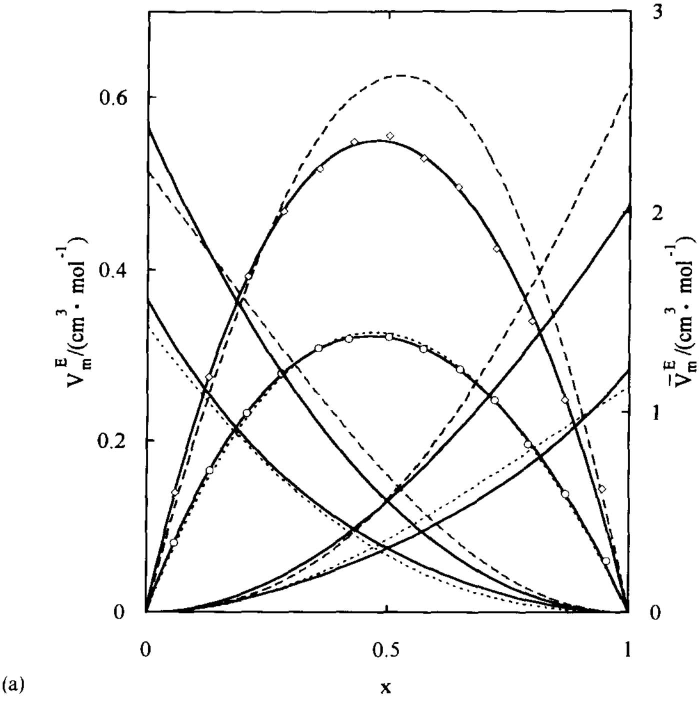

Fig. 1. Excess molar volumes V^E_m and excess partial molar volumes $\bar{V}^E_{m_i}$ at 308.15 K of (a), {xc-$(CH_2)_pO + (1-x)$c-$(CH_2)_6$} and (b), {xc-$(CH_2)_pO + (1-x)C_6H_5CH_3$}: ◇, $p = 4$; ○, $p = 5$; ——, calculated from Eq. (1) with parameters from Table 2; -----, predicted values using the PFP theory.

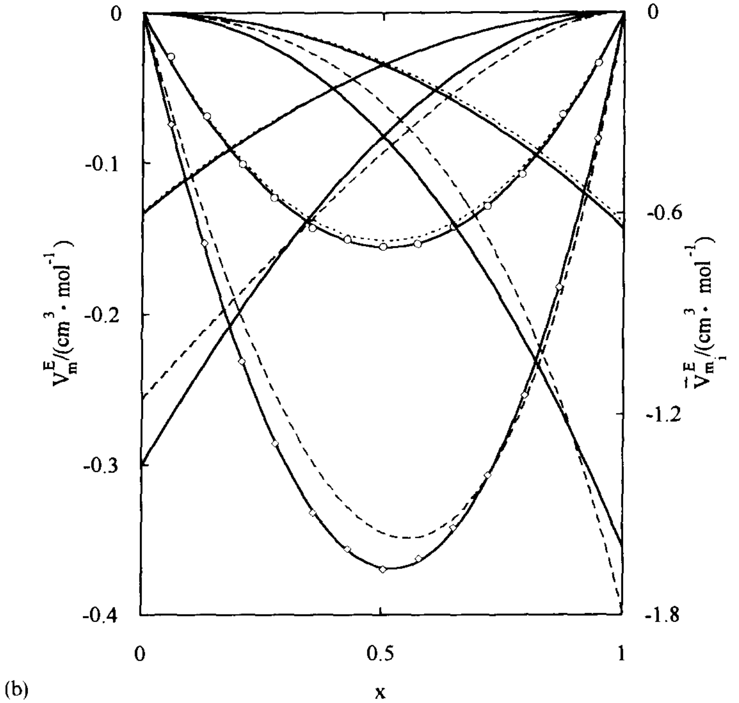

Fig. 1. (*Continued*).

To illustrate the aforementioned characteristics Figs. 1(a) and 1(b) show the experimental results at the temperature 308.15 K for the systems $\{x\text{c-}(CH_2)_pO + (1-x)\text{c-}C_6H_{12}\}$ and $\{x\text{c-}(CH_2)_pO + (1-x)C_6H_5CH_3\}$, respectively. Partial excess molar volumes, $\bar{V}_{m_i}^E$, are also included in these figures.

In order to apply the Prigogine–Flory–Patterson molecular model it is necessary to take into account that this model uses only one adjustable parameter, the interaction parameter χ_{12}, but it uses other characteristic parameters of the pure compounds directly related to the liquid physical properties. Table 6 contains the characteristic parameters for the pure compounds which were obtained from the thermal expansion

Table 6
Parameters for pure components

Compound	$v^*/(cm^3\,mol^{-1})$	$p^*/(J\,cm^{-3})$
c-$(CH_2)_4O$	63.13	562
c-$(CH_2)_5O$	76.79	663 [6]
c-C_6H_{12}	84.31	540
$C_6H_5CH_3$	84.56	613

Table 7
Experimental and predicted excess molar volumes at $x = 0.5$ using PFP theory and interaction parameters χ_{12}

System	T/K	χ_{12}/(J cm^{-3})	$V^E_{m_{exp}}$/cm^3 mol^{-1}	$V^E_{m_{PFP}}$/cm^3 mol^{-1}
xc-(CH$_2$)$_4$O + (1 − x)c-C$_6$H$_{12}$	288.15	37.00	0.5286	0.5296
	298.15	37.00	0.5356	0.5752
	308.15	37.00	0.5480	0.6241
xc-(CH$_2$)$_5$O + (1 − x)c-C$_6$H$_{12}$	288.15	24.00	0.3059	0.2796
	298.15	24.00	0.3091	0.3024
	308.15	24.00	0.3212	0.3260
xc-(CH$_2$)$_4$O + (1 − x)C$_6$H$_5$CH$_3$	288.15	−19.45	−0.3716	−0.2924
	298.15	−19.45	−0.3695	−0.3180
	308.15	−19.45	−0.3686	−0.3448
xc-(CH$_2$)$_5$O + (1 − x)C$_6$H$_5$CH$_3$	288.15	−12.00	−0.1648	−0.1300
	298.15	−12.00	−0.1621	−0.1403
	308.15	−12.00	−0.1559	−0.1515

coefficients, α, calculated in this work, and from the isothermal compressibility, κ_T, calculated by using the Lydersen–Grenkorn–Hougen method [30].

The interaction parameter χ_{12} was calculated from excess molar enthalpies at $T = 298.15$ K obtained from the literature [12, 31, 32], and Table 7 reports the values of these parameters together with the V^E_m predictions by PFP model at $x = 0.5$ compared with our experimental results. The agreement between experimental and predicted values is excellent, specially for the mixtures {THF or THP + cyclohexane}, where the discrepancies are smaller than 12 per cent. Nevertheless the PFP model predicts for the mixtures {THF or THP + toluene} a decrease of V^E_m with temperature, whereas the experimental results show that the excess volumes increase with increasing temperature. These results can be explained taking into account that, for these mixtures, the specific solute– solvent interaction is stronger than the interactions present in the pure liquids, a situation which goes beyond the applicability of the model.

Figs. 1(a) and (b) show the excess molar volumes and partial excess molar volumes predicted by the PFP model for the mixtures: {xc-(CH$_2$)$_p$O + (1 − x)c-C$_6$H$_{12}$} and {xc-(CH$_2$)$_p$O + (1 − x)C$_6$H$_5$CH$_3$} at the temperature 308.15 K.

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