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APPLICATION OF PRIGOGINE-FLORY-PATTERSON THEORY TO EXCESS MOLAR VOLUMES OF BINARY LIQUID MIXTURES OF {METHYL TERT BUTYL ETHER (MTBE) + ALCOHOLS} AT DIFFERENT TEMPERATURES AND ATMOSPHERIC PRESSURE

APLICAÇÃO DA TEORIA PRIGOGINE-FLORY-PATTERSON AO VOLUME MOLAR EXCESSO DE SOLUÇÕES LÍQUIDAS BINÁRIAS DE {METIL TERC BUTIL ÉTER (MTBE) + ALCOÓIS} A DIFERENTES TEMPERATURAS E PRESSÃO ATMOSFÉRICA

H. E. HOGA[1] and R. B. TORRES[1,*]

[1] Centro Universitário FEI, Departamento de Engenharia Química, São Bernardo do Campo-SP, Brasil

[*]*Autor Correspondente: Centro Universitário FEI, Departamento de Engenharia Química, Avenida Humberto de Alencar Castelo Branco, 3972, 09850-901, São Bernardo do Campo, São Paulo, Brasil, Telefone: +55-11-5353-2900 (r.2075)*
e-mail addressl: belchior@fei.edu.br (R. B. Torres).

A R T I C L E I N F O

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p a l a v r a s - c h a v e
Metil terc butil éter
Álcoois
Volume molar excesso
Teoria Prigogine-Flory-Patterson

k e y w o r d s
Methyl tert butyl ether
Alcohols
Excess molar volume
Prigogine-Flory-Patterson theory

A B S T R A C T

In the present study, experimental data of excess molar volumes (V_m^E) of binary liquid mixtures of methyl tert butyl ether (MTBE) + methanol, or + ethanol, or + 1-propanol, or + 2-propanol, or + 1-butanol, or + 1-pentanol, or + 1-hexanol have been used to test the applicability of the Prigogine-Flory-Patterson theory (PFP) as a function of composition at different temperatures and atmospheric pressure. According to the model, interactional contribution is the most important one to explain the behavior. It may be observed that the PFP theory reproduces the main features of the experimental data by using only one fitted parameter adjusted. Good agreements between the experimental results and the theory were obtained for all the systems studied.

R E S U M O

No presente estudo, dados experimentais de volume molar excesso (V_m^E) de soluções líquidas binárias de metil terc butl éter (MTBE) + metanol, ou + etanol, ou + 1-propanol, ou + 2-propanol, ou + 1-butanol, ou + 1-pentanol, ou + 1-hexanol foram usados para testar a aplicabilidade da Teoria Prigogine-Flory-Patterson (PFP Theory), como função da composição a diferentes temperaturas e pressão atmosférica. De acordo com o modelo, a contribuição interacional é a mais importante para descrever o comportamento do V_m^E. Foi observado que a Teoria PFP reproduz os dados experimentais usando apenas um parâmetro ajustável. Para todos os sistemas estudados foi obtida uma boa concordância entre os resultados experimentais e a Teoria.

1. INTRODUCTION

Excess properties have been a qualitative and quantitative way to predict ideality deviation of liquid binary mixtures. Moreover, excess molar volume has been used to develop and to test solution models and theories. The Prigogine–Flory–Patterson theory (PFP theory) (BARBE and PATTERSON, 1980; VAN and PATETERSON, 1982), born as a modification of Flory's theory (PRIGOGINE, 1957; FLORY et al., 1964a,b), has been widely used to analyze excess thermodynamic properties for different kinds of mixtures, including polar components. According to the Prigogine-Flory-Patterson theory (PFP theory), excess molar volumes calculations include three contributions: (i) interactional contribution which is proportional to the Flory parameter; (ii) the free volume contribution which arises from the dependence of the reduced volume upon the reduced temperature as a result of the difference between the degree of expansion of the two components, and (iii) the P* contribution which depends both on the differences of internal pressure and differences of reduced volumes of the components.

In previous paper (HOGA and TORRES, 2011) we have presented experimental results involved volumetric and viscometric properties of binary mixtures of methyl tert butyl ether (MTBE) + alcohols. We have also presented the applicability of the ERAS model for these results. The scope of the present work is to test the applicability of the PFP theory on data of excess molar volumes of binary mixtures of methyl tert butyl ether (MTBE) + methanol, or + ethanol, or + 1-propanol, or + 2-propanol, or + 1-butanol, or + 1-pentanol, or + 1-hexanol as a function of composition at the temperatures of 293.15, 298.15, 303.15 and 308.15 K and atmospheric pressure. The text of the entire manuscript must be typed in single-line spacing, but double spacing must be given between paragraphs. The page format should be A4 (210 mm × 297 mm), in the "portrait" orientation mode, divided in two columns with narrow margin. The font must be Times New Roman, with size 12 in the main title and size 10 in the secondary title (second language); size 10 must also be given in the first-, second- and third-order headers, and also in the text; size 8 must be given in the authors' reference notes below the titles.

2. PRIGOGINE-FLORY-PATTERSON THEORY

The excess molar volume is defined by:

$$V_m^E = x_1 M_1 (1/\rho - 1/\rho_1) + x_2 M_2 (1/\rho - 1/\rho_2) \quad (1)$$

in which M_1, M_2, ρ_1, ρ_2 represent the molar masses and densities of the pure components, respectively, and ρ is the density of liquid solution.

The V_m^E was calculated by means of the PFP theory using the following equation:

$$\frac{V_m^E}{x_1 V_1^* x_2 V_2^*} = \frac{\overbrace{(\tilde{V}^{1/3}-1)\tilde{V}^{2/3}\psi_1\theta_2(\chi_{12}/P_1^*)}^{\chi_{12}\ contribution}}{\left((4/3)\tilde{V}^{-1/3}-1\right)} - \frac{\overbrace{(\tilde{V}_1-\tilde{V}_2)^2\left((14/9)\tilde{V}^{-1/3}-1\right)\psi_1\psi_2}^{\tilde{V}\ contribution}}{\left((4/3)\tilde{V}^{-1/3}-1\right)\tilde{V}} + \frac{\overbrace{(\tilde{V}_1-\tilde{V}_2)(P_1^*-P_2^*)\psi_1\psi_2}^{P^*\ contribution}}{P_2^*\psi_1+P_1^*\psi_2} \quad (2)$$

The thermal expansion coefficient αi is used to compute the reduced volume of pure component i by equation:

$$\tilde{V}_i = \left(\frac{1+(4/3)\alpha_i T}{1+\alpha_i T}\right)^3 \quad (3)$$

The $\tilde{V}$ of the solution is obtained by iterative solution of the Flory equation of state in the zero pressure limit form:

$$\tilde{T} = \frac{\tilde{V}^{1/3}-1}{\tilde{V}^{4/3}} \quad (4)$$

The characteristic volume is $V_i^* = V_i/\tilde{V}_i$ and the characteristic pressure is given by:

$$P_i^* = T\tilde{V}_i^2\alpha_i/\kappa_i \quad (5)$$

where κ_i is the isothermal compressibility and V_i is the molar volume of component i.

Here, the molecular contact energy fraction of the components is given by:

$$\Psi_1 = 1 - \Psi_2 = \phi_1 P_1^*/(\phi_1 P_1^* + \phi_2 P_2^*) \quad (6)$$

with the hard-core volume fractions of the components defined by:

$$\phi_1 = 1 - \phi_2 = x_1 V_1^*/(x_1 V_1^* + x_2 V_2^*) \quad (7)$$

The molecular surface fraction of the component 2 is given by:

$$\theta_2 = \frac{\phi_2(S_2/S_1)}{\phi_1+\phi_2(S_2/S_1)} \quad (8)$$

where S_2/S_1 is the molecular surface/volume ratio for the components determined by Bondi's method (BONDI, 1964).

3. RESULTS AND DISCUSSIONS

The values of parameters of the pure components required in the PFP theory were obtained using Flory's formalism (PRIGOGINE, 1957; FLORY et al., 1964a,b) and are listed in Table 1 (APENDIX A).

In order to obtain it is necessary to find the interactional parameter, χ_{12}, which was obtained by fitting the theory to experimental values of excess molar volume for each one of the binary system under study. The calculated equimolar values of the three contributions to and interactional parameter are shown in Table 2 (APENDIX A).

Figures 1-7 show the composition dependence of theoretical and experimental values for the systems studied. The experimental values are negative over the entire composition range and it becomes more negative when temperature increases.

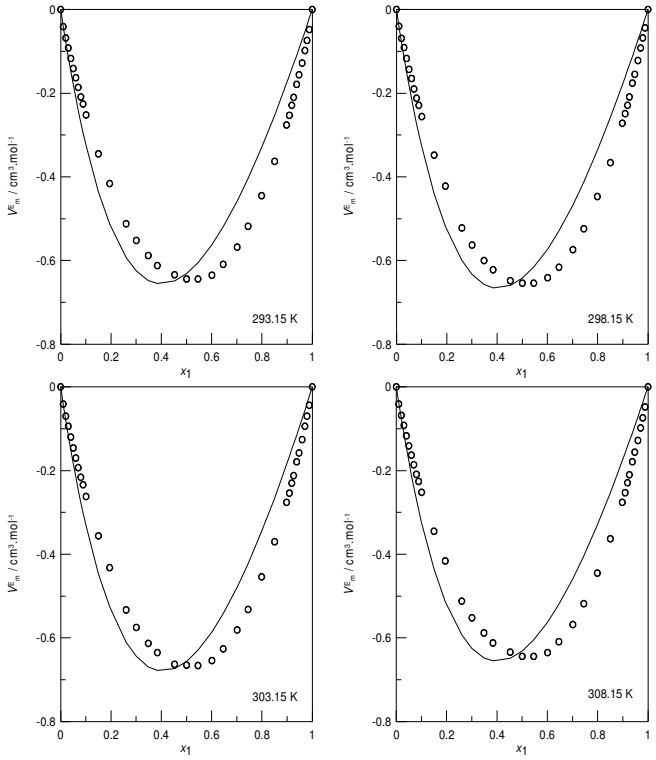

Figure 1 – Excess molar volume as a function of mole fraction of MTBE for the {x1 MTBE + (1-x1) methanol) mixture: ○, experimental (HOGA and TORRES, 2011); —, calculated by using PFP theory.

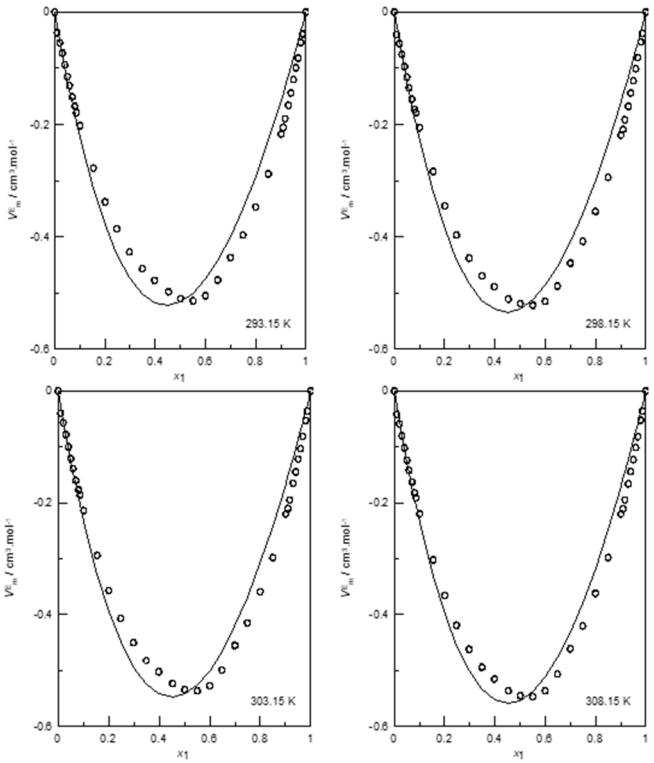

Figure 2 – Excess molar volume as a function of mole fraction of MTBE for the {x1 MTBE + (1-x1) ethanol) mixture: ○, experimental (HOGA and TORRES, 2011); —, calculated by using PFP theory.

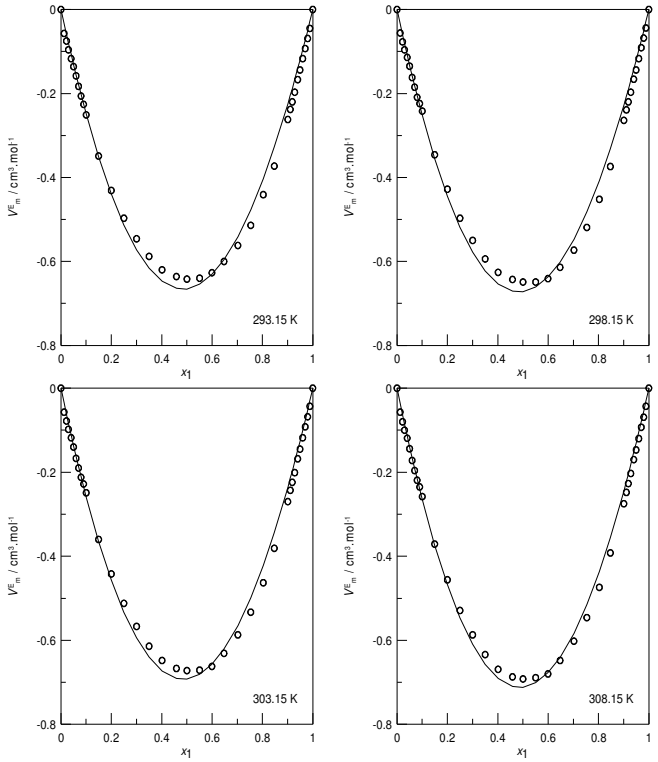

Figure 3 – Excess molar volume as a function of mole fraction of MTBE for the {x1 MTBE + (1-x1) 1-propanol) mixture: ○, experimental (HOGA and TORRES, 2011); —, calculated by using PFP theory.

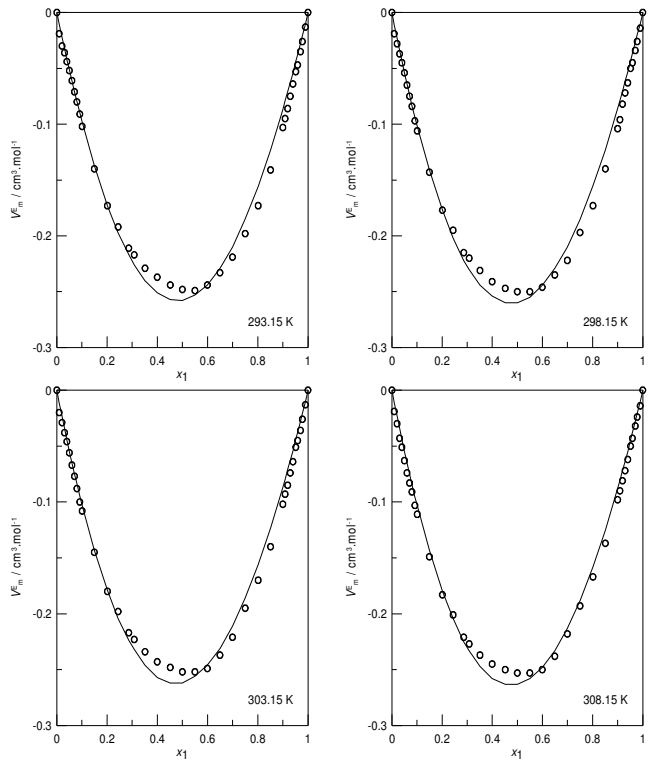

Figure 4 – Excess molar volume as a function of mole fraction of MTBE for the {x1 MTBE + (1-x1) 2-propanol) mixture: ○, experimental (HOGA and TORRES, 2011); —, calculated by using PFP theory.

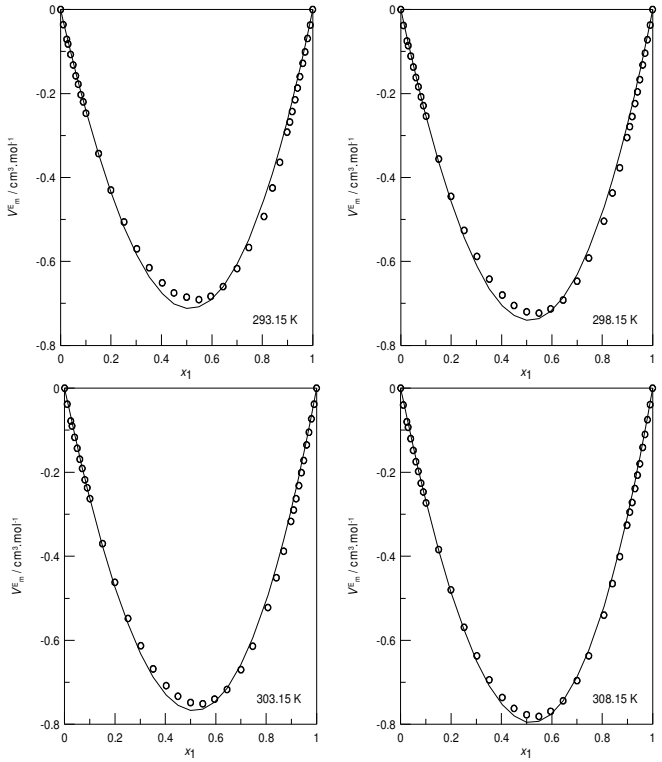

Figure 5 – Excess molar volume as a function of mole fraction of MTBE for the {x1 MTBE + (1-x1) 1-butanol) mixture: ○, experimental (HOGA and TORRES, 2011); —, calculated by using PFP theory.

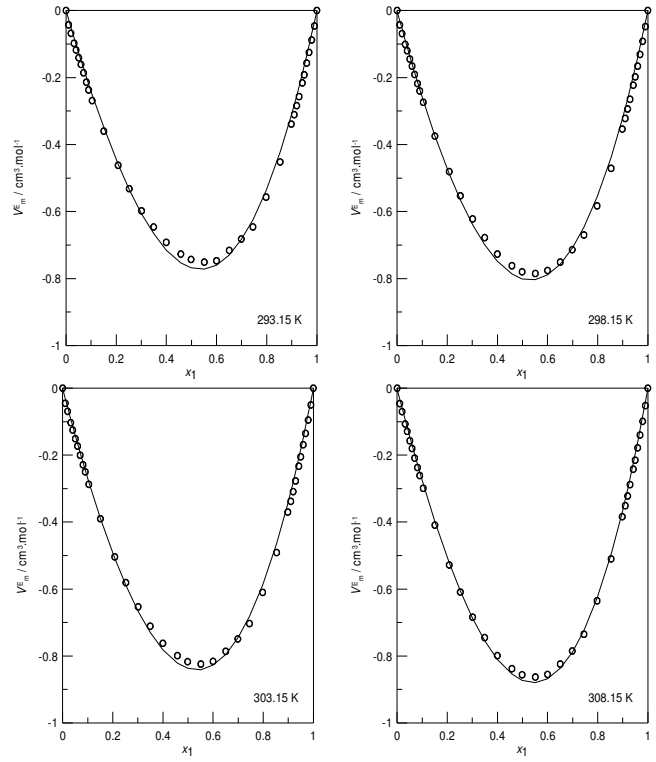

Figure 6 – Excess molar volume as a function of mole fraction of MTBE for the {x1 MTBE + (1-x1) 1-pentanol) mixture: ○, experimental (HOGA and TORRES, 2011); —, calculated by using PFP theory

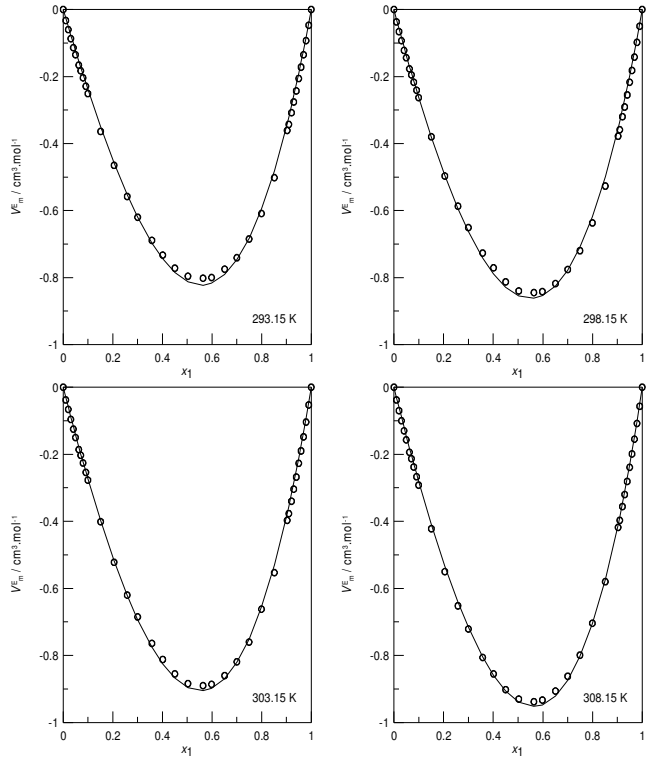

Figure 7 – Excess molar volume as a function of mole fraction of MTBE for the {x1 MTBE + (1-x1) 1-hexanol) mixture: ○, experimental (HOGA and TORRES, 2011); —, calculated by using PFP theory.

An analysis of each of the three contributions to shows that the interactional contribution is always negative and it seems to be the most important to explain the behavior of the systems studied. This contribution has the same sign as Flory's parameter χ_{12}. The free volume effect, which is a measure of geometrical accommodation, is positive and it seems to have little significance for the systems studied. The third contribution, due to differences in internal pressure and in reduced volume of the components, seems also to have little influence for the studied systems.

For all mixtures, the calculated curves agree very well with the experimental data. However, deviations have occurred for systems containing methanol and ethanol. The theoretical basis of the PFP theory gives rise to some restrictions in its application. For example, hydrogen bonds, strong dipolar interactions and complex formation are excluded from this model. Although the theory does not consider all the possible interactions existent in the mixtures under study, we may conclude that the theoretical results show that the PFP theory reproduces the main features of the experimental data by using only one fitted parameter to describe V_m^E.

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APENDIX A

Table 1 – Parameters of the pure components used in PFP theory calculations.

Component	T(K)	P^* (J cm^{-3})	V (cm^{3}mol^{-1})	V^* (cm^{3}mol^{-1})	β (x10^4 K^{-1})	κ (x10^4 MPa^{-1})	S (nm^{-1})
MTBE	293.15	525.1[p]	119.26[p]	89.38[p]	14.75[p]	14.45 [p]	14.71[a]
	298.15	485.1[p]	119.91[a]	90.29[b]	14.20[b]	15.39[b]	14.71[a]
	303.15	445.1[p]	120.56[p]	91.2[p]	13.65[p]	16.32[p]	14.71[a]
	308.15	405.1[b]	121.21[b]	92.10[b]	13.10[b]	17.26[b]	14.71[a]
Methanol	293.15	424.3[c]	40.47[c]	32.06[c]	11.80[c]	12.10[c]	16.49[f]
	298.15	423.1[d]	40.72[d]	32.13[e]	11.89[d]	12.48[d]	16.49[f]
	303.15	418[e]	41.02[e]	32.23[e]	11.95[e]	12.92[e]	16.49[f]
	308.15	415.5[p]	41.28[p]	32.31[p]	12.03[p]	13.32[p]	16.49[f]
Ethanol	293.15	422.7[d]	58.37[d]	46.8[d]	11.2[d]	11.05[d]	15.22[g]
	298.15	413[h]	58.66[h]	46.90[h]	11.20[h]	11.53[h]	15.22[g]
	303.15	403.9[d]	58.99[d]	47.1[d]	11.2[d]	11.95[d]	15.22[g]
	308.15	397.6[i]	59.33[i]	47.25[g]	11.16[i]	12.30[i]	15.22[g]
1-Propanol	293.15	428.4[c]	74.78[c]	60.90[c]	10.2[c]	9.55[c]	14.90[j]
	298.15	414.1[d]	75.12[h]	61.09[h]	10.2[d]	10.06[h]	14.90[j]
	303.15	399.8[c]	75.54[c]	61.30[c]	10.2[c]	10.57[c]	14.90[j]
	308.15	385.5[p]	75.9[p]	61.5[p]	10.2[p]	11.08[p]	14.90[j]
2-Propanol	293.15	399.0[c]	76.58[c]	61.97[c]	10.53[c]	10.81[c]	14.87[f]
	298.15	380[h]	76.95[h]	62.31[h]	10.60[h]	11.30[h]	14.87[f]
	303.15	383[k]	77.40[c]	62.04[k]	10.68[a]	11.82[a]	14.87[f]
	308.15	375[p]	77.8[p]	62.23[p]	10.75[p]	12.32[p]	14.87[f]
1-Butanol	293.15	432.6[c]	91.56[c]	75.62[c]	9.24[c]	9.34[c]	14.56[c]
	298.15	396.7[d]	91.98[d]	75.7[d]	9.32[d]	9.42[d]	14.56[c]
	303.15	412.8[c]	92.43[c]	75.77[c]	9.39[c]	9.49[c]	14.56[c]
	308.15	404.4[a]	92.86[p]	75.84[p]	9.46[p]	9.56 [p]	14.56[c]
1-Pentanol	293.15	447.2[p]	108.22[p]	88.95[p]	8.6[p]	8.55[p]	14.33[n]
	298.15	436.1[m]	108.7[m]	89.2[m]	9.000[l]	8.820[l]	14.33[n]
	303.15	425[n]	109.18[n]	89.45[n]	9.39[n]	9.09[n]	14.33[n]
	308.15	413.9[p]	109.66[p]	89.7[p]	9.78[p]	9.36[p]	14.33[n]
1-Hexanol	293.15	381[p]	125.68[p]	104.92[p]	8.08[p]	8.09[p]	14.18[n]
	298.15	405[h]	125.26[h]	104.27[h]	8.58[h]	8.36[h]	14.18[n]
	303.15	429[n]	125.84[n]	103.62[n]	9.08[n]	8.63[n]	14.18[n]
	308.15	453[p]	126.42[p]	102.97[p]	9.58[p]	8.9[p]	14.18[n]

[a]BICH et al. (1999), [b]DOMANSKA (1997), [c]TORRES et al. (2003), [d]FUNKE et al. (1989), [e]JAIN et al. (2009), [f]REZANOVA et al. (2000), [g]GARCIA-MIAJA et al. (2008), [h]HEINTZ (1985), [i]BENDER and HEINTZ (1993), [j]MOHREN and HEINTZ (1997), [k]OSWAL (2004) , [l]GALVÃO and FRANCESCONI (2006), [m]HOLMAN and CASANOVA (1989), [n]Ref.[21], [o]Calculated, [p]Estimated.

Tabel 2 - The three contribution of V_m^E from PFP theory for equimolar composition and interaction parameter χ_{12} for binary systems at different temperatures.

T / K	χ_{12} / J·cm^{-3}	Interactional (cm^3·mol^{-1})	Free volume (cm^3·mol^{-1})	P^* (cm^3·mol^{-1})
x_1 MTBE + (1-x_1) Methanol				
293.15	-49.55	-0.6625	0.0463	0.0775
298.15	-44.35	-0.6274	0.0309	0.0165
303.15	-41.29	-0.6178	0.0182	-0.0197
308.15	-39.71	-0.6267	0.0078	-0.0357
x_1 MTBE + (1-x_1) Ethanol				
293.15	-33.52	-0.5295	0.0914	0.1042
298.15	-29.15	-0.4880	0.0699	0.0297
303.15	-26.12	-0.4613	0.0499	-0.0302
308.15	-24.12	-0.4484	0.0336	-0.0714
x_1 MTBE + (1-x_1) 1-Propanol				
293.15	-35.13	-0.6086	0.1874	0.1304
298.15	-29.99	-0.5512	0.1534	0.0325
303.15	-26.95	-0.5238	0.1209	-0.0477
308.15	-24.93	-0.5117	0.0904	-0.1098
x_1 MTBE + (1-x_1) 2-Propanol				
293.15	-18.19	-0.3342	0.1578	0.2342
298.15	-12.72	-0.2466	0.1220	0.1088
303.15	-9.05	-0.1853	0.0880	0.0116
308.15	-6.82	-0.1469	0.0583	-0.0583
x_1 MTBE + (1-x_1) 1-Butanol				
293.15	-41.39	-0.8005	0.3200	0.4089
298.15	-31.24	-0.6222	0.2664	0.1487
303.15	-23.87	-0.4887	0.2144	-0.0639
308.15	-19.06	-0.4009	0.1645	-0.2292
x_1 MTBE + (1-x_1) 1-Pentanol				
293.15	-41.50	-0.8373	0.4565	0.5255
298.15	-28.68	-0.5924	0.3383	0.1302
303.15	-21.37	-0.4526	0.2336	-0.1507
308.15	-18.65	-0.4059	0.1449	-0.3219
x_1 MTBE + (1-x_1) 1-Hexanol				
293.15	-43.59	-0.9183	0.5973	0.7026
298.15	-27.94	-0.5973	0.4341	0.1766
303.15	-19.04	-0.4144	0.2910	-0.1909
308.15	-16.26	-0.3616	0.1735	-0.4038