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Excess molar volumes and enthalpies of binary mixtures containing furan and toluene, 1-octanol or n-hexane at temperatures up to 383.15 K and pressure up to 1.6 MPa.

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Abstract

Densities of pure furan, toluene, 1-octanol, n-hexane and, of binary liquid mixtures containing furan, has been measured from 303.15 K to 383.15 K at pressures up to 1.6 MPa, using a vibrating tube densimeter. Excess molar volumes have been calculated from the densities with an average standard uncertainty $0.02 \text{ cm}^3 \cdot \text{mol}^{-1}$. Excess molar enthalpies of the binary mixtures were measured at temperatures ranging from 313.15 to 383.15 K at 0.5 MPa and/or 1.0 MPa, using flow mixing calorimeter. The average standard uncertainty on the whole measurements is less than 1%. The excess molar properties derived from experimental data were correlated using a Redlich-Kister polynomial functions, NRTL activity coefficient model and Prigogine Flory Patterson modelling is described and used to correlate the data.

Keywords: furan, toluene, 1-octanol, n-hexane, experimental excess properties, modelling

Introduction

Due to the depletion of fossil resources, green chemistry has now become a real alternative to petrochemicals. Lignocellulosic biomass (LCB) refers to plant biomass that is composed mainly of lignin and cellulose (wood residues, cereal straw and forestry waste) [1]. Currently, this biomass is the most important source of renewable energy and the only renewable source of carbon. It can provide for about 10% of total energy consumption worldwide (IEA Statistics, 2021). However, this cannot be considered as the optimal use of LCB resources because much of this consumption concerns firewood-based heating and cooking. This biomass is also playing a major role in the chemical sectors as a substitution material. Nevertheless, the major part of the annual production of biomass (220 billion tonnes per year) is still underexploited and, there remains considerable scope for the development of LCB value chains for the production of energy, chemicals, polymers and materials.

Molecules derived from lignocellulosic biomass pyrolysis belong to a variety of complex oxygen compound families [2]. The main families identified are carbonyls, sugars, oxygenated aromatics and furans. The thermodynamic behavior of these molecules is not well known because the models and methods traditionally used for hydrocarbons fail to return it. Indeed, these molecules are the site of complex molecular interactions. Consequently, experimental determination of excess thermodynamic properties will be necessary. These properties will be required during new product design chemicals and development of new production processes from lignocellulosic material.

This paper focus on the furan as a derived molecule obtained from the pyrolysis of the LCB. Furan can be used as a precursor for the synthesis of pharmaceutical molecules [3] as well as fungicides, herbicides or disinfectants [4]. To the best of our knowledge, only few data for Vapour-Liquid and Liquid-Liquid Equilibrium of binary and ternary mixtures containing furan are available in the open literature ([5], [6] and [7]). Apparent Henry's law constants of Furan in various n-Alkanes and alcohols were obtained by Hajiw *et al.*[8] and, the excess enthalpy for the binary mixture {n-hexane-furan} were measured at 298.15K and 303.15K by M. D. Guillen [9]. As a result, a study of excess properties has been realized for the binary mixtures constituted with furan and n-hexane, toluene or 1-octanol. These molecules were selected as potential solvent for liquid-liquid extraction.

1 Experimental

Chemicals.

The chemicals used are listed in table 1 together with molecular formula, CAS number, suppliers, purity given by the supplier and molecular weights. All the compounds were used without further purification.

Table 1 Chemicals used for experimental work

Chemical name	Molecular Formula	CAS number	Supplier	purity	Molecular weight g.mol ⁻¹
Furan	C ₄ H ₄ O	110-00-9	Acros Organics	99.0%	68.07
n-hexane	CH ₃ (CH ₂) ₄ CH ₃	110-54-3	Acros Organics	99.0%	86.18
Toluene	C ₆ H ₅ CH ₃	108-88-3	Fischer Scientific	99.0%	92.14

Properties studied

In this paper, two excess molar properties have been investigated: excess molar volumes and excess molar enthalpies. The excess property Y^E , Eq. (1), represents the difference between the value Y measured in the real solution and the value Y^{id} calculated for an ideal solution, at the same conditions of pressure, temperature, and composition, [10]. To measure excess properties, the system will have to be in liquid phase before and after mixing. The normal boiling points are: 304.2 K for furan, 383.5 K for toluene and, 341.8 K for n-hexane [11]. To remain in liquid phase at investigated temperatures [303.15 K -383.15 K], our experiments were performed at 1.65 MPa for the densimetric measurements and, at 0.5 and 1.0 MPa for the enthalpy measurements.

$$Y^E = Y - Y^{id} \quad (1)$$

Preparation of the binary mixtures.

For densimetric measurements, 45 g to 50 g of binary mixtures were prepared by weight in Schott Duran flasks (50 ml) using a Mettler Toledo AE163 balance with a precision of 0.1 mg. the remaining gas space after preparation was flushed with nitrogen before hermetically closing the flasks. The uncertainty on the molar fraction is estimated to be better than 10^{-4} .

For flow calorimetric measurements, binary mixtures are prepared directly in situ. The uncertainty on the composition is obtained from a calculation of propagation of error including the uncertainty on the density and on the volume flow rate of pure components. The relative uncertainty on volume flow rate, using an ISCO pump (Model 100 DM) is 0.03%. Considering an uncertainty of 10^{-2} kg.m⁻³ on pure component density, the final uncertainty on the molar fraction of the mixture is estimated to be $2 \cdot 10^{-4}$.

Volumetric technique

Densities were obtained at 3 temperatures, namely 303.15 K, 353.15 K and 383.15 K, using a vibrating tube densimeter DMA HPM from Anton Paar. The experiments were performed in a flow regime. The temperature inside the densimeter was controlled using a cryostat model F12-MA from Julabo, with a precision of 0.05 K. Its short-term temperature stability (over one experiment) was ± 0.01 K while the long-term temperature fluctuation can reach 0.03 K. The pressure was maintained stable to 0.05 MPa using a back-pressure regulator from Swagelok (KPB1L0D412P200B0 model) and was measured by a Drück electronic (PMP4010 model) pressure gauge with a precision of 0.03 MPa.

The density of mixtures, ρ_m , is derived from periods of vibration using Eq. (2)

$$\rho_m = \rho_{ref} + K \cdot (\tau_m^2 - \tau_{ref}^2) \quad (2)$$

where τ_m and τ_{ref} are the period of vibration when flowing solution (*m*) or reference fluid (*ref*) respectively. ρ_{ref} is the density of the reference fluid and K is a calibration constant. This calibration constant K was determined by measurements of water and NaCl solutions with well-known densities. The relative uncertainty in the calibration constant is about 0.3%. The reference density of water was calculated with the equation of Hill [12], the reference density of NaCl solutions was obtained from the recommendations of Archer [13]. The stability of the measured periods τ_m and τ_{ref} was typically $5 \cdot 10^{-6}$ ms at 303.15 K and $1 \cdot 10^{-5}$ ms at higher temperatures. After calculation of propagation of error, the uncertainty in the density is found to be about 10^{-2} kg.m³.

The density of pure furan was measured with water as reference fluid considering Eq. (2). For the other pure compounds as well as for mixtures, the reference fluid was furan. The measurements are performed at a constant flow rate of 0.1 ml.min⁻¹. The overall setup of the experiment is represented in the Fig. 1. Furan is first circulating into the vibrating tube densimeter using an DM 100 ISCO high pressure syringe pump (flow line (1)). The second pure compound (or the mixture) is introduced in a sample loop prior to experiment. After registering the value of the period of vibration for furan (τ_{ref}), the second fluid (or mixture) is then introduced (flow line (2)), and the period of vibration (τ_m) is registered.

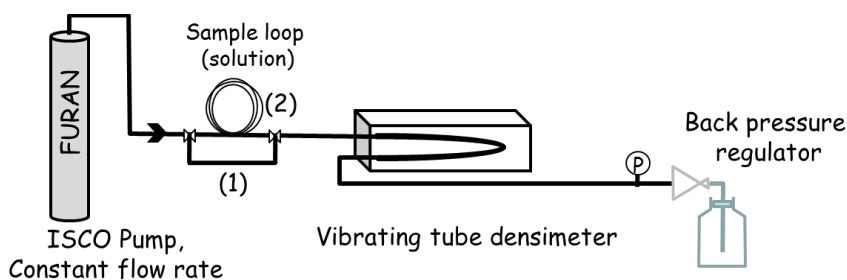


Fig. 1 Schematic representation of the experimental setup for density measurements.

Excess molar volumes V^E are calculated from the experimental density data using Eq. (3)

$$V^E = \left[\frac{x_{fur}M_{fur} + x_2M_2}{\rho} \right] - \frac{x_{fur}M_{fur}}{\rho_{fur}} - \frac{x_2M_2}{\rho_2} \quad (3)$$

where x is the molar fraction, ρ the density and M the molar mass; subscript “*fur*” refers to furan and “2” refers to the second pure compound. The estimated average total uncertainty, including molality calculations, and vibrating tube period noise and reproducibility on the excess molar volume is 0.01 cm³.mol⁻¹.

Calorimetric technique

The excess molar enthalpies are obtained by measuring thermal effect due to the mixing of furan with a second compound, using a Setaram BT2.15 heat conduction differential calorimeter. The fluids mix in a flow mixing cell developed originally in the laboratory [14]. The thermal effect (heat power) is detected by a calibrated thermopile. Measurements were carried out in flow mode at constant temperature and pressure. The excess molar enthalpies are measured for different molar fractions of furan, obtained by changing the molar flow rates ration (\dot{n}_{fur}/\dot{n}_2). The two fluids (furan and compound 2) are supplied by two high-pressure syringe pumps (Isco Model 100 DM). These two

pumps are regulated at a constant temperature of 303.15 K, using a JULABO thermostatic bath (model FP 89) that permit a temperature control with a stability of 0.1K. Molar fraction of furan is calculated from molar flow rates (\dot{n}) using Eq. (4).

$$x_{fur} = \frac{\dot{n}_{fur}}{\dot{n}_{fur} + \dot{n}_2} \text{ with } \dot{n} = \frac{\rho \cdot \dot{v}}{M} \quad (4)$$

The molar flow rates (\dot{n}) were calculated from the pump volume flow rates (\dot{v}) using the densities (ρ) and the molar mass of the fluids (M). The total volume flow rate arriving at the mixing point was maintain constant to a value of 0.5 ml.min⁻¹.

The molar excess enthalpy H^E is derived from the heat power of mixing and the molar flow rates \dot{n} (mol.s⁻¹) as indicated in Eq. (5); the calorimetric signal ΔS (mV) is converted into heat power using a calibration constant K (mV·mW⁻¹).

$$H^E / Jmol^{-1} = \frac{\Delta S}{K(\dot{n}_{fur} + \dot{n}_2)} \quad (5)$$

The calorimetric signal ΔS represents the difference between the signal recorded during mixing and a baseline signal recorded when only furan is flowing into the circuit. This signal is varying between 100mV and 800 mV, depending on the binary mixture composition for furan + 1-Octanol and furan + n-hexane. The calibration constant K is determined using the reference data for excess enthalpies of {ethanol-water} system recommended by Ott *et al.* [15, 16]. Considering the uncertainties on flow rates, thermopile calibration K and calorimetric signal stability and temperature fluctuations, the relative expanded uncertainty on enthalpies are lower than 5 % for very dissymmetric mixtures (large differences in compressibility or molecular weight of the compounds, or large differences in the flow rates of the pumps). For the compounds studied in this paper this uncertainty is reduced to 1%.

2 Results and discussions

In this section, the density, the excess molar volume and the excess molar enthalpy of binary mixtures will be presented at different pressure and temperature. The excess molar properties (volume and enthalpy) will be correlated using the Redlich-Kister (RK) polynomial function and the NRTL activity coefficient model as implemented in the Simulis thermodynamic software developed by Prosim® (France).

2.1 Density of pure compounds

The density and molar volume of pure compounds at 303.15 K and pressures up to 2.1MPa are presented in Table 2.

Table 2 Densities (ρ) and molar volumes (V^M) of pure compounds at 303.15 K and pressures up to 2.1MPa

T / K	p / MPa	$\rho / \text{kg.m}^{-3}$				$V^M / \text{cm}^3.\text{mol}^{-1}$			
		Toluene	Furan	n-Hexane	1-Octanol	Toluene	Furan	n-Hexane	1-Octanol
303.15	0.1*	857.20	***	649.90	817.72	107.53	***	132.56	159.26
	Lower literature value**	856.9		649.4	817.2				
	Upper literature value**	860.4		655.9	818.4				
303.15	1.13	857.98	924.93	651.35	818.48	107.39	73.59	132.31	159.11
303.15	1.63	858.42	925.53	651.89	818.80	107.34	73.55	132.20	159.05

303.15	2.13	858.87	926.15	652.44	819.14	107.28	73.50	132.09	158.98
353.15	1.65	804.25	844.24	583.29	772.04	114.57	80.75	147.75	168.68
383.15	1.65	779.22	799.21	571.33	759.02	118.25	85.18	150.83	171.57

*extrapolated value from Tait's equation; ** literature values from Dortmund Data Bank; *** gas phase at this temperature.

Standard uncertainties u are: $u(\rho) = 2.10^{-2} \text{ kg}\cdot\text{m}^3$ for furan, n-hexane, toluene and 1-octanol at 303.15 K; $u(\rho) = 5.10^{-2} \text{ kg}\cdot\text{m}^3$ for 1-octanol at 353 K; $u(\rho) = 7.10^{-2} \text{ kg}\cdot\text{m}^3$ for 1-octanol at 383 K; $u(V^M) = 0.01 \text{ cm}^3\cdot\text{mol}^{-1}$

The molar volumes were fitted to a Tait's equation [17] as presented in Eq. (6); the parameters $v(0,T)$, $B(T)$ and C calculated at 303.15 K are reported in Table 3.

$$V^M(p, T) = v(0, T) \left\{ 1 - C \ln \left[1 + \frac{p}{B(T)} \right] \right\} \quad (6)$$

Table 3 Parameters for Tait's equation [17], at 303.15 K.

Compound	$v(0, T) / \text{cm}^3\cdot\text{mol}^{-1}$	C	B / MPa	SD*
furan	73.69	0.4439	354.2	0.0045
Toluene	107.49	$-5.0426 \cdot 10^{-3}$	-6.527	0.002
n-Hexane	132.59	0.0189	9.740	0.0021
1-Octanol	159.26	0.4542	546.6	0.0045

*Standard Deviation $SD = \sqrt{\frac{\sum (v - v_{est})^2}{n}}$

The densities at 0.1 MPa reported in Table 2 were derived from Eq. (6) to be compared to available literature values. More than 30 references are available for the three compounds studied. The minimum and the maximum literature values for density are reported in the Table 2, at 303.15 K and 0.1 MPa. In all cases our experimental value is included in the maximum-minimum interval. The molar volume of pure compounds increases mostly linearly in our temperature domain; the evolution is more important for n-hexane.

2.2 Experimental results for the binary mixtures

Furan + n-hexane

Because of furan volatility, it was necessary to run experiment above 0.1 MPa. In order to test the influence of pressure on excess enthalpies, measurements at 353.15 K were realized at 0.5 and 1.0 MPa. The results show that the difference in molar excess enthalpy values is within experimental uncertainty.

The densities and excess molar volumes of binary mixtures furan + n-hexane were obtained at 303.15, 353.15 and 383.15 K and 1.6 MPa. The excess enthalpies were measured at 313.15, 353.15 K and 383.15 K and, pressures 0.5 MPa and 1.0 MPa. Experimental data are reported in Table 4 and represented in Fig. 2. As it was shown that there is no influence of the pressure on excess enthalpies within the range studied, values obtained at 0.5 MPa and 1.0 MPa were considered as a single set of data for RK correlation at 353.15 K.

Table 4 Volumetric and calorimetric data obtained for the binary mixture furan + n-hexane.

Densities (ρ) and excess molar volumes (V^E) of binary mixture furan + n-hexane at 1.6 MPa.								
x_{furan}	ρ ($\text{kg}\cdot\text{m}^{-3}$)	V^E ($\text{cm}^3\cdot\text{mol}^{-1}$)	x_{furan}	ρ ($\text{kg}\cdot\text{m}^{-3}$)	V^E ($\text{cm}^3\cdot\text{mol}^{-1}$)	x_{furan}	ρ ($\text{kg}\cdot\text{m}^{-3}$)	V^E ($\text{cm}^3\cdot\text{mol}^{-1}$)
303.15 K			353.15 K			383.15 K		
0	651.89	0	0.0000	583.29	0.00	0.0000	571.33	0.00
0.1428	672.55	0.47	0.1274	600.66	0.44	0.1050	582.08	0.85
0.3934	718.16	0.95	0.4127	648.88	1.25	0.2041	594.07	1.41
0.3454	708.35	0.89	0.7556	740.13	0.92	0.2970	607.55	1.66
0.6010	768.74	1.00	0.8886	791.68	0.42	0.4999	642.66	2.00
0.7706	823.35	0.72	1.0000	844.24	0.00	0.6092	666.46	1.92
0.9211	885.77	0.29				0.7063	691.77	1.63
0.9555	902.55	0.15				0.8058	722.42	1.17
1	925.53	0				0.9075	758.87	0.66
						1.0000	799.21	0.00

Excess molar enthalpies of binary mixture furan + n-hexane.							
x_{fur}	H^E (J.mol ⁻¹)	x_{fur}	H^E (J.mol ⁻¹)	x_{fur}	H^E (J.mol ⁻¹)	x_{fur}	H^E (J.mol ⁻¹)
313.15 K, 0.5 MPa		353.15 K, 0.5 MPa		353.15 K, 1 MPa		383.15 K, 1 MPa	
0	0	0	0	0	0	0	0
0.1599	569 ± 4	0.1464	479 ± 4	0.1588	505 ± 2	0.1588	442 ± 2
0.2044	704 ± 5	0.1600	514 ± 2	0.2031	632 ± 3	0.2031	548 ± 2
0.2551	847 ± 5	0.2046	640 ± 3	0.2981	871 ± 3	0.2981	743 ± 3
0.2999	949 ± 5	0.3000	865 ± 3	0.3891	999 ± 4	0.3891	871 ± 4
0.3910	1100 ± 5	0.3637	970 ± 4	0.4855	1078 ± 4	0.4855	947 ± 3
0.4876	1185 ± 5	0.3913	1006 ± 4	0.5311	1091 ± 4	0.5311	953 ± 4
0.5332	1194 ± 5	0.4878	1086 ± 4	0.6295	1061 ± 6	0.607	949 ± 8
0.6313	1162 ± 6	0.5334	1095 ± 4	0.6295	1068 ± 4	0.6295	951 ± 6
0.6315	1137 ± 9	0.6316	1062 ± 5	0.6295	1065 ± 7	0.6295	927 ± 4
0.6315	1147 ± 5	0.7059	983 ± 5	0.7182	947 ± 5	0.6295	931 ± 6
0.7199	1021 ± 4	0.7200	925 ± 4	0.8717	563 ± 2	0.7182	831 ± 4
0.8106	799 ± 5	0.8108	762 ± 5	0.9281	340 ± 2	0.8094	657 ± 3
0.8727	598 ± 3	0.8727	559 ± 4	1	0	0.8717	492 ± 2
0.9286	366 ± 3	0.9287	350 ± 2			0.9281	302 ± 2
1	0	1	0			1	0

Standard uncertainties u are $u(V^E) = 0.01 \text{ cm}^3\cdot\text{mol}^{-1}$; $u(x) = 0.0001$.

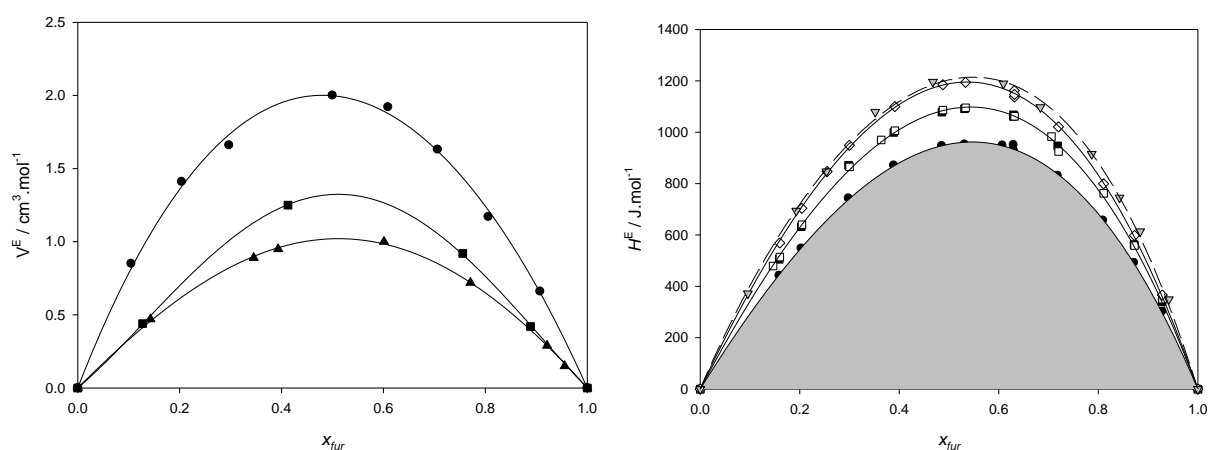


Fig. 2 Furan + n-hexane binary system; left: excess molar volumes at 1.65 MPa; \blacktriangle : 303.15 K; \blacksquare : 353.15 K; \bullet : 383.15 K. right: excess molar enthalpies at \diamond : 313.15 K, 0.5 MPa; \square : 353.15 K, 0.5 MPa; \bullet : 353.15 K, 1.0 MPa; \bullet : 383.15 K, 1.0 MPa. \blacktriangledown : 303.15 K, 0.1 MPa [Guillen et al. [9]]. The full lines are RK correlations for our data, dashed line is RK correlation of literature [Guillen et al. [9]].

A Redlich-Kister (RK) correlation was first use to describe the excess molar properties for each temperature using Eq. (7).

$$X^E = x_2(1 - x_2) \sum A_n(1 - 2x_2)^n \quad (7)$$

Where X is Volume or Enthalpy, A_n are the adjustable coefficients of the equation, and n the number of parameters to be considered. The parameters are given in table 5 and Table 6.

The average standard error of the estimates is 0.02 cm³.mol⁻¹ for the volumetric properties and less than 3% for the calorimetric properties.

Table 5 Excess molar volume Redlich-Kister parameters for binary mixtures at pressure $p = 1.65$ MPa

T / K	A ₀	A ₁	A ₂	A ₃	SD*
Furan – n-Hexane					
303.15	4.0805	0.2074	-0.3879		0.01
353.15	5.5922	0.3302	-2.0069		0.01
383.15	7.9925	-0.5985	0.3741		0.04
Furan – Toluene					
303.15	-0.1738	0.1565	0.6465		
353.15	-0.3213	-0.02731	0.08688		
383.15	-0.2743	-0.1688	-0.2352		
Furan – 1-Octanol					
303.15	1.3393	0.7241	-0.3206		0.02
353.15	1.1539.10 ⁻⁴	1.2499	-0.4081		0.03
353.15	-0.01536	1.6555	-0.3386	-0.9965	0.01
383.15	-0.9228	0.2099	0.5983		0.02

*Standard Deviation $SD = \sqrt{\frac{\sum_n (V_{exp}^E - V_{Calc}^E)^2}{n}}$

Table 6 Excess molar enthalpies Redlich-Kister parameters for binary mixtures with pressure between 0.1 and 1 MPa.

T / K	A ₁	A ₂	A ₃	SD**
Furan – n-Hexane				
303.15*	4815.70	847.970	514.966	7.2
313.15	4754.60	706.468	74.2019	6.0
353.15	4357.94	763.296	83.1453	8.5
383.15	3813.27	725.836	37.6165	6.4
Furan – Toluene				
313.15	219.235	-31.961	51.1446	2
353.15	195.717	-58.779	6.17613	2
383.15	153.245	4.4940	-2.08364	4
Furan – 1-Octanol				
313.15	5870.00	3718.04	3098.19	48
353.15	7060.40	3603.94	2539.81	26
383.15	6573.37	2683.14	975.98	35

*RK correlation for literature values [Guillen et al. [9]]; ***Standard Deviation $SD = \sqrt{\frac{\sum_n (H_{exp}^E - H_{Calc}^E)^2}{n}}$

From these experimental data and those found in the open literature [9], it has been noticed that for this polar - non-polar mixture, the excess molar enthalpies and volumes are positive for the entire composition range and for all temperature studied (Fig. 2). In fact, the attractive interactions between molecules of different compounds are, on average, weaker than those between molecules of the same compound. The excess molar enthalpy is a decreasing function of the temperature; meanwhile, the excess molar volume is an increasing function of the temperature.

Furan + 1-octanol

The densities, molar volumes and enthalpies of the binary mixture furan + 1-octanol are presented in Table 7, and plotted in Fig. 3. The experimental excess enthalpies are positive for the entire composition range.

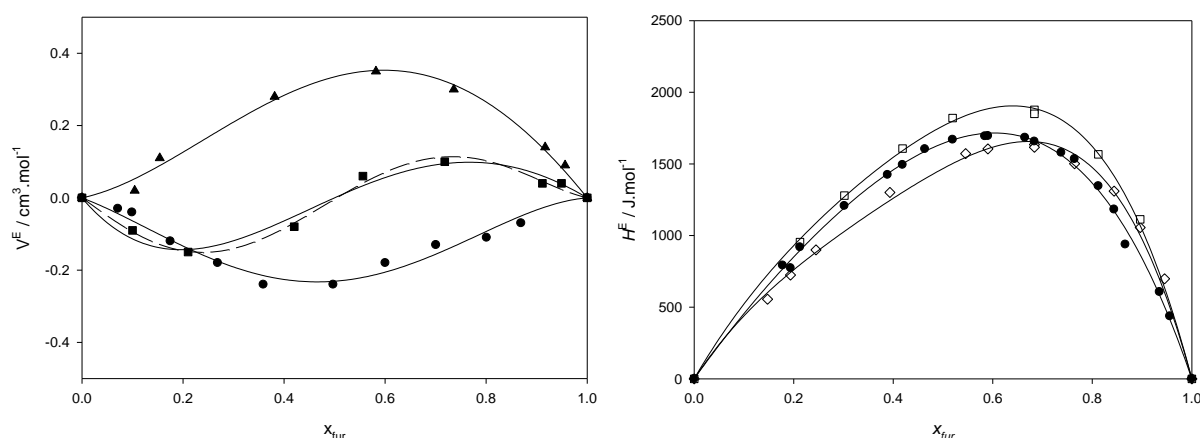


Fig. 3 Furan + 1-octanol binary system; left: excess molar volumes at 1.65 MPa; \blacktriangle : 303.15 K; \blacksquare : 353.15 K; \bullet : 383.15 K. right: excess molar enthalpies at \diamond : 313.15 K, 0.5 MPa; \square : 353.15 K, 0.5 MPa; \bullet : 383.15 K, 1.0 MPa. The full lines are RK correlations with 3 parameters. The dashed line is the RK correlation with 4 parameters.

Table 7 Volumetric and calorimetric data obtained for the binary mixture furan + 1-octanol.

Densities (ρ) and excess molar volumes (V^E) of binary mixture furan + 1-octanol at 1.6 MPa.								
x_{furan}	ρ ($\text{kg}\cdot\text{m}^{-3}$)	V^E ($\text{cm}^3\cdot\text{mol}^{-1}$)	x_{furan}	ρ ($\text{kg}\cdot\text{m}^{-3}$)	V^E ($\text{cm}^3\cdot\text{mol}^{-1}$)	x_{furan}	ρ ($\text{kg}\cdot\text{m}^{-3}$)	V^E ($\text{cm}^3\cdot\text{mol}^{-1}$)
303.15 K			353.15 K			383.15 K		
0	818.8		0	772.04		0.0000	759.02	
0.1043	824.13	0.02	0.1000	776.10	-0.09	0.0712	760.65	-0.03
0.1539	826.49	0.11	0.2100	780.95	-0.15	0.0991	761.27	-0.04
0.3814	840.6	0.28	0.4201	791.11	-0.08	0.1750	763.42	-0.12
0.5818	857.85	0.35	0.5560	798.65	0.06	0.2688	766.16	-0.18
0.7359	876.19	0.30	0.7180	810.89	0.10	0.3591	769.06	-0.24
0.9168	906.48	0.14	0.9113	831.66	0.04	0.4973	773.71	-0.24
0.9562	914.91	0.09	0.9491	836.57	0.04	0.6004	777.33	-0.18
1	925.53		1	844.24		0.7006	781.54	-0.13
						0.8010	786.67	-0.11
						0.8691	790.42	-0.07
						1.0000	799.21	
Excess molar enthalpies of binary mixture furan + 1-octanol.								
x_{furan}	H^E (J.mol $^{-1}$)	x_{furan}	H^E (J.mol $^{-1}$)	x_{furan}	H^E (J.mol $^{-1}$)	x_{furan}	H^E (J.mol $^{-1}$)	
313.15 K, 0.5 MPa		353.15 K, 0.5 MPa		383.15 K, 1 MPa				
0	0	0	0	0	0	0.6837	1657 \pm 10	
0.1474	556 \pm 5	0.2127	954 \pm 4	0.1777	792 \pm 5	0.7375	1579 \pm 9	

0.1936	724 ± 5	0.3018	1279 ± 5	0.1937	774 ± 5	0.7643	1535 ± 8
0.2448	900 ± 6	0.4188	1607 ± 5	0.2127	919 ± 6	0.8121	1346 ± 7
0.3934	1301 ± 6	0.5194	1820 ± 6	0.3018	1208 ± 9	0.7375	1579 ± 9
0.5456	1572 ± 7	0.6837	1877 ± 7	0.3887	1424 ± 7	0.7643	1535 ± 8
0.5903	1605 ± 6	0.6837	1850 ± 6	0.4188	1494 ± 7	0.8121	1346 ± 7
0.6837	1635 ± 10	0.8121	1567 ± 5	0.4637	1604 ± 7	0.8439	1183 ± 6
0.6837	1616 ± 7	0.8963	1113 ± 4	0.5194	1670 ± 8	0.8664	938 ± 10
0.7643	1501 ± 6	1	0	0.5842	1694 ± 8	0.9351	607 ± 4
0.8438	1310 ± 6			0.5904	1696 ± 9	0.9558	437 ± 3
0.8963	1056 ± 4			0.6646	1684 ± 9	1	0
0.9453	698 ± 4						
1	0						

Standard uncertainties u are $u(V^E) = 0.01 \text{ cm}^3 \cdot \text{mol}^{-1}$; $u(x) = 0.0001$.

Meanwhile, for the excess molar volume, we notice that even so the values are weak, and lower than $0.4 \text{ cm}^3 \cdot \text{mol}^{-1}$, they change from positive to negative when increasing temperature. This can be explained by a change in the molecular interactions in the solution. At low temperature, the interactions between molecules of same species are stronger while at the highest temperature, intermolecular interactions are predominant, leading to a contraction of the solution. This is probably linked with the change in the evolution of the excess enthalpy that goes through a maximum before decreasing at higher temperature. The RK correlations were also realized for this system, with 3 parameters for both properties. However, for the excess molar volumes at 353.15 K, due to the wave form of the curve, the standard state deviation is poor and a fit with 4 parameters was needed.

Furan + toluene

The excess molar volume and enthalpies of the binary mixture furan + toluene are presented in Table 8 and plotted in Fig. 4.

Table 8 Volumetric and calorimetric data obtained for the binary mixture furan + toluene.

Densities (ρ) and excess molar volumes (V^E) of binary mixture furan + toluene at 1.6 MPa.								
x_{furan}	ρ ($\text{kg} \cdot \text{m}^{-3}$)	V^E ($\text{cm}^3 \cdot \text{mol}^{-1}$)	x_{furan}	ρ ($\text{kg} \cdot \text{m}^{-3}$)	V^E ($\text{cm}^3 \cdot \text{mol}^{-1}$)	x_{furan}	ρ ($\text{kg} \cdot \text{m}^{-3}$)	V^E ($\text{cm}^3 \cdot \text{mol}^{-1}$)
	303.15 K			353.15 K			383.15 K	
0	858.42	0	0.0000	804.26	0.00	0	779.20	0
0.0580	860.78	0.04	0.1087	807.64	-0.03	0.2148	782.80	-0.04
0.1204	864.17	-0.00	0.3204	814.63	-0.05	0.4098	786.50	-0.08
0.1149	863.97	-0.01	0.4907	820.99	-0.07	0.6071	790.30	-0.07
0.3309	875.70	-0.03	0.8662	837.62	-0.06	0.8055	794.64	-0.05
0.5058	886.35	-0.03	1.0000	844.24	0.00	1	799.21	0
0.7034	900.14	-0.02						
0.9555	920.68	0.05						
1	925.53	0						
Excess molar enthalpies of binary mixture furan + toluene.								
x_{fur}	H^E (J.mol ⁻¹)	x_{fur}	H^E (J.mol ⁻¹)	x_{fur}	H^E (J.mol ⁻¹)			
	313.15 K, 0.5 MPa		353.15 K, 0.5 MPa		383.15 K, 1 MPa			
0	0	0	0	0	0			
0.1395	18 ± 3	0.1395	27 ± 3	0.1395	6 ± 3			
0.1795	23 ± 4	0.1795	30 ± 3	0.2673	25 ± 3			
0.2034	27 ± 4	0.2259	39 ± 3	0.3045	31 ± 3			
0.2259	30 ± 4	0.2672	43 ± 3	0.3536	34 ± 3			
0.2672	32 ± 3	0.3536	50 ± 2	0.3847	35 ± 3			
0.3044	38 ± 3	0.4218	53 ± 4	0.4218	42 ± 5			
0.3536	40 ± 3	0.4476	53 ± 4	0.4477	45 ± 3			

0.4126	46 ± 4	0.4930	54 ± 2	0.4931	40 ± 3
0.4476	48 ± 4	0.5933	53 ± 6	0.5933	34 ± 3
0.4930	47 ± 3	0.5933	55 ± 3	0.6142	33 ± 5
0.5933	50 ± 5	0.6863	52 ± 2	0.6864	32 ± 2
0.6863	46 ± 3	0.7848	45 ± 3	0.773	23 ± 2
0.7848	41 ± 4	0.8537	32 ± 2	0.7848	26 ± 3
0.8537	29 ± 3	0.9173	21 ± 2	0.8537	19 ± 2
0.9173	19 ± 3	1	0	0.9173	20 ± 3
1	0			0.9292	13 ± 2
				1	0

Standard uncertainties u are $u(V^E) = 0.01 \text{ cm}^3 \cdot \text{mol}^{-1}$; $u(x) = 0.0001$.

For furan + toluene, the experimental excess enthalpies are positive for the entire composition range and their values are very weak with a maximum value $50 \text{ J} \cdot \text{mol}^{-1}$. The experimental excess molar volumes are close to zero (lower than $0.1 \text{ cm}^3 \cdot \text{mol}^{-1}$). This behaviour indicates that the properties of the mixture are close to the ideal properties.

The RK correlation was done with 3 parameters, but they are not significant due to the weakness of the excess properties.

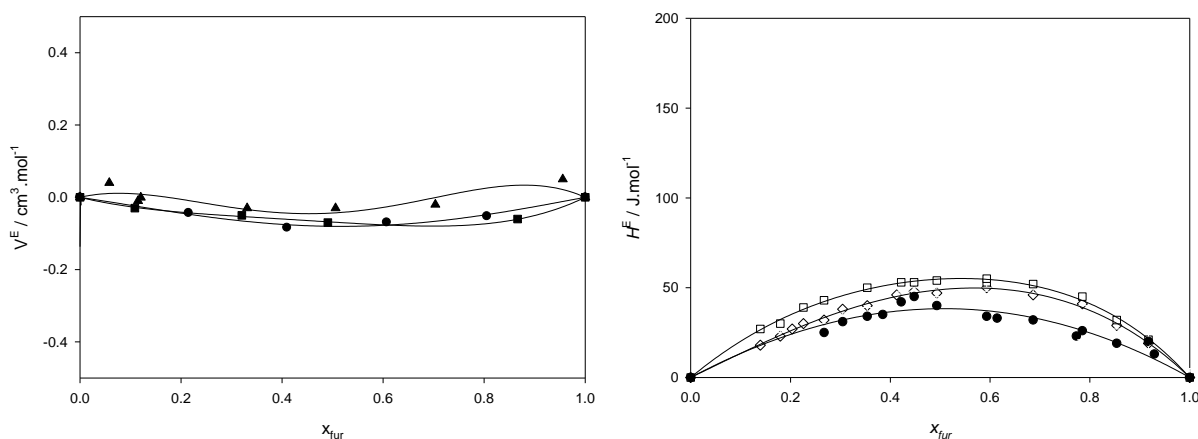


Fig. 4 Furan + Toluene binary system; left: excess molar volumes at 1.65 MPa; \blacktriangle : 303.15 K; \blacksquare : 353.15 K; \bullet : 383.15 K. right: excess molar enthalpies at \diamond : 313.15 K, 0.5 MPa; \square : 353.15 K, 0.5 MPa; \bullet : 383.15 K, 1.0 MPa. The lines are RK correlations with 3 parameters.

2.3 NRTL correlation of excess molar enthalpies

The NRTL activity coefficient model was applied for binary mixtures furan + n-hexane and furan + 1-octanol. The binary mixture furan + toluene was not considered as the excess enthalpies are nearly equal to zero. The non-randomness parameter α was adjusted to a constant value of 0.17. The interaction parameters are temperature dependant and have been adjusted for each temperature using Simulis Thermodynamics software, from Prosim[®]. As the pressure has no significant effect on the excess molar enthalpy and, as the parameters are not pressure dependant, the data obtained at 0.5 and 1.0 MPa for the same temperature were treated as a single set of data. The NRTL parameters are given in Table 9 for both systems furan + n-hexane and furan + 1-octanol.

Table 9 Interaction parameters of the NRTL activity coefficient model for excess molar enthalpies of binary mixtures furan + n-hexane and furan + 1-octanol with $\alpha = 0.17$.

T / K	a_{12}	a_{21}	*AAD (%)
Furan + n-hexane			
313.15 K	1005.18	455.96345	0.8
353.15 K	1030.26	287.06292	0.8
383.15 K	974.58	149.93793	0.7
Furan + 1-octanol			
313.15 K	2922.15	835.402577	2
353.15 K	2858.46	812.992373	0.7
383.15 K	2206.00	460.572079	1.4

* $\text{AAD} = (100/N) \sum |(H_{cal}^E - H_{exp}^E) / H_{exp}^E|$, N is the number of data points, subscript cal corresponds to calculated value and, exp corresponds experimental value.

A good agreement (Fig 5) between models and experimental results is observed. It can be seen that NRTL model is able to accurately represent the excess molar enthalpies of the two binary systems studied. The AAD is less than 1% for both binary mixtures. The NRTL correlation will be used in the next part to compare the different binary mixtures at a given temperature.

2.4. Comparison of excess properties of binary mixtures at given temperature

The excess molar volumes and enthalpies are plotted in Fig. 5 as function of the furan molar fraction, at 303.15 K and 313.15 K for V^E and H^E , respectively. The correlation shows a good agreement with the data as mentioned in part 3.3. The thermodynamic excess properties are very close to zero for the binary mixture furan + toluene (Fig. 5). The excess molar volume V^E is larger for n-hexane + furan than for the other mixtures while the largest excess molar enthalpy is reached by furan + 1-octanol mixture. The maximum of the thermodynamic properties is displaced to the highest molar fraction of furan when it is mixed with 1-octanol: V^E is maximum when $x_{\text{furan}} \sim 0.6$ and, H^E is maximum when $x_{\text{furan}} \sim 0.7$. This behaviour is linked to specific intermolecular interactions between the alcohol group and le furan, that tends to skewed the properties toward mixtures rich in furan. For the other systems the maximum is located around $x_{\text{furan}} \sim 0.5$ because of more simple molecular interactions.

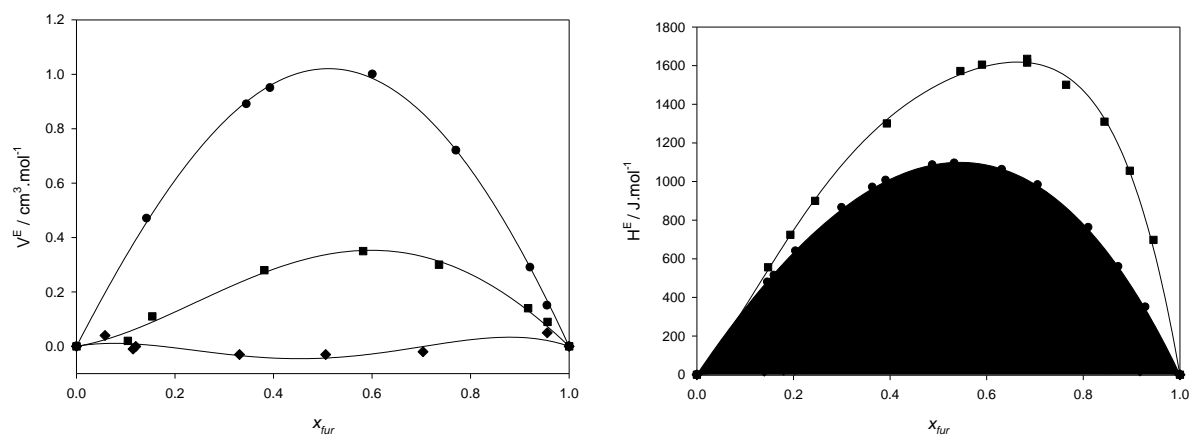


Fig. 5 Comparison of excess properties of binary systems with furan (■ : 1-octanol; ● : n-hexane; ◆ : toluene); left: excess molar volumes of at 303.15 K and 1.65 MPa; Lines are RK correlations and right: excess molar enthalpies at 313.15 K and 0.5 MPa; The lines are NRTL correlations for furan + 1-octanol and furan + n-Hexane systems. RK fits are used for furan + toluene system.

3 Prigogine Flory Patterson modelling

In order to analyse the excess molar enthalpy, it is possible to use the Prigogine Flory Patterson model [18]. As the pressure effect is not significant in our experimental data, we apply the PFP model for the two binary systems furan + n-hexane and furan + 1-octanol. We do not use this model for the binary system furan + toluene due to the low value of the excess enthalpy. The particularity of this model is to decompose the excess property into several contributions. Concerning excess molar enthalpy, it exists mainly two contributions. We suppose that there is no chemical reaction between the chemicals. It is important to remind that this model was originally used to analyse the excess thermodynamic properties of non-polar mixture and was extended to polar mixtures. We can cite the recent work of Coquelet et al. [19] on the excess volume of similar binary systems.

The PFP model describes the interaction between the chemical species and the expression of the excess molar enthalpy is reported in Eq. (8).

$$\frac{H^E}{x_1 u_1^* + x_2 u_2^*} = (-\tilde{U} + \tilde{T} \tilde{C} p) \psi_1 \theta_2 \frac{x_{12}}{p_1^*} - \frac{1}{2} \left(\frac{\tilde{v}_1 - \tilde{v}_2}{\frac{\partial \tilde{U}}{\partial \tilde{T}}} \right)^2 \frac{\partial^2 \tilde{U}}{\partial \tilde{T}^2} \psi_1 \psi_2 \quad (8)$$

For the excess molar enthalpy, the two main contributions are:

- Interactional contribution: this contribution is proportional to the Flory parameter. This parameter can be calculated using solubility parameter and reflects the energy change during the contact between the unlike molecules. In previous work [20] it has been considered that this parameter can be expressed as a function of the volume fraction.
- Free volume contribution or curvature contribution: it is link to configurational entropy. It can be attributed to the difference in the degree of thermal expansion between the molecules.

The equation of state used in the PFP model is defined by the Eq. (9)

$$\frac{\tilde{p} \tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{v} \tilde{T}} \quad (9)$$

with $\tilde{p} = p/p^*$, $\tilde{v} = v/v^*$ and $\tilde{T} = T/T^*$. T^* , p^* and v^* are the characteristics parameters obtained directly from the thermodynamic properties of the pure liquid. The tilde refers to an average reduced quantity. Concerning the volume $\tilde{v} = \psi_1 \tilde{v}_1 + \psi_2 \tilde{v}_2$ with $\tilde{v}_i = \left((1 + \frac{4}{3} \alpha_i T) / (1 + \alpha_i T) \right)^3$, where α_i is the thermal expansion coefficient. The reduced temperature is determined considering the PFP EoS using Eq. (10-11).

$$\tilde{T} = \frac{\tilde{v}^{1/3} - 1}{\tilde{v}^{4/3}} \quad (10)$$

$$\tilde{v}^{1/3} - 1 = \frac{\alpha T / 3}{1 + \alpha T} \quad (11)$$

The characteristic pressure can be calculated using Eq. (12)

$$p_i^* = \frac{\alpha_i}{\kappa_{Ti}} T \tilde{v}_i^2 \quad (12)$$

where α is the thermal expansion coefficient and κ_T , the isothermal compressibility. The reduced configurational energy is determined by $\tilde{U}_i = -1/\tilde{v}_i$ and the characteristic configurational energy is $U_i^* = p_i^* v_i^*$. Concerning the heat capacity, we can estimate the reduced heat capacity at constant pressure following Eq. (13).

$$\tilde{C}_{pi} = \frac{3\tilde{v}_i^{1/3}}{4 - 3\tilde{v}_i^{1/3}} \quad (13)$$

The contact energy fraction in Eq. (14) is derived from hardcore volume fraction ϕ_i (Eq. (15)), surface fraction θ_i (Eq. (16)) and, molecular surface/volume ratios s_i .

$$\psi_1 = 1 - \psi_2 = \frac{\phi_1 p_1^*}{\phi_1 p_1^* + \phi_2 p_2^*} \quad (14)$$

$$\phi_1 = 1 - \phi_2 = \frac{x_1 v_1^*}{x_1 v_1^* + x_2 v_2^*} \quad (15)$$

$$\theta_2 = \frac{\phi_2 s_2}{\phi_1 s_1 + \phi_2 s_2} \quad (16)$$

The ratio s_1/s_2 can be approximated by the ratio of pure molar volume $(v_2^*/v_1^*)^{1/3}$, leading to Eq. (17) for surface fraction.

$$\theta_2 = 1 + \frac{\phi_1}{\phi_2} \left(\frac{v_2^*}{v_1^*} \right)^{-1/3} \quad (17)$$

The reduced configurational energy for the mixture is $\tilde{U} = \psi_1 \tilde{U}_1 + \psi_2 \tilde{U}_2$. The reduced heat capacity at constant pressure for the mixture is $\tilde{C}_p = \psi_1 \tilde{C}_{p1} + \psi_2 \tilde{C}_{p2}$. Consequently, using the PFP equation of state and the different defined variables, the expression of the excess volume can be determined (Eq. (18)).

$$\frac{H^E}{x_1 u_1^* + x_2 u_2^*} = \left(\frac{1}{\tilde{v}} + \frac{T}{4/3\tilde{v}^{-1/3} - 1} \right) \psi_1 \theta_2 \frac{x_{12}}{p_1^*} - \frac{\left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}_2} \right)^2 2/9\tilde{v}^{-2/3}}{4/3\tilde{v}^{-1/3} - 1} \psi_1 \psi_2 \quad (18)$$

Unity of H^E is imposed by the choice of unity of v_i^* and v_i . Temperature is in Kelvin. The choice of unity of pressure (among other p_i^*) imposed the unity of χ_{12} .

We will use the parameters defined by Coquelet et al. [20]. We remind that for a pure component, the isothermal compressibility κ_{T_i} is related to the isentropic compressibility κ_S via the Maxwell's relations $\kappa_{T_i} = \kappa_S + \alpha^2 v_i^\circ T / C_p$ where v_i [m³/mol] is the molar volume of the compound i , κ_S is the isentropic compressibility ($\kappa_S = -1/v(\partial v/\partial p)_S$) [Pa⁻¹]. The molar volume, heat capacity, thermal expansion, isentropic compressibility and isothermal compressibility used [21] are calculated at atmospheric pressure using a second order polynomial function of temperature (Eq. (19)). The polynomial parameters a , b and c are reported in Table 10.

$$F(T) = aT^2 + bT + c \quad (19)$$

Table 10 Values of the second order polynomial expression (Eq. (18)) for pure compounds.

Property F	a	b	c
1-Octanol			
v / cm ³ .mol ⁻¹	1.70.10 ⁻⁰⁴	0.032	133.8
α / K ⁻¹	-2.12.10 ⁻⁰⁹	2.695.10 ⁻⁰⁶	2.3.10 ⁻⁰⁴
C_p / J.mol ⁻¹ .K ⁻¹		1.070	-14.51
χ_S / Pa ⁻¹	1.56.10 ⁻¹⁴	-5.3.10 ⁻¹²	8.7.10 ⁻¹⁰

χ_T / Pa^{-1}	$1.5822 \cdot 10^{-14}$	$-4.9808 \cdot 10^{-12}$	$8.594 \cdot 10^{-10}$
n-Hexane			
$v / \text{cm}^3 \cdot \text{mol}^{-1}$	$4.29 \cdot 10^{-04}$	-0.0730	115.1
α / K^{-1}	$-1.090 \cdot 10^{-08}$	$1.109 \cdot 10^{-05}$	$-9.48 \cdot 10^{-04}$
$C_p / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$1.45 \cdot 10^{-03}$	-0.493	213.40
χ_S / Pa^{-1}	$7.45 \cdot 10^{-14}$	$-3.15 \cdot 10^{-11}$	$4.09 \cdot 10^{-09}$
χ_T / Pa^{-1}	$7.685 \cdot 10^{-14}$	$-2.929 \cdot 10^{-11}$	$3.604 \cdot 10^{-09}$
Furan			
$v / \text{cm}^3 \cdot \text{mol}^{-1}$	$2.47 \cdot 10^{-04}$	-0.0388	62.7
α / K^{-1}	$-1.185 \cdot 10^{-08}$	$1.162 \cdot 10^{-05}$	$-9.24 \cdot 10^{-04}$
$C_p / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$6.2 \cdot 10^{-04}$	-0.159	107.03
χ_S / Pa^{-1}	$5.20 \cdot 10^{-14}$	$-2.25 \cdot 10^{-11}$	$2.92 \cdot 10^{-09}$
χ_T / Pa^{-1}	$5.473 \cdot 10^{-14}$	$-2.032 \cdot 10^{-11}$	$2.452 \cdot 10^{-09}$

The PFP model was applied for the 2 binary systems at 313.15, 353.15 and 383.15K. In order to adjust the χ_{12} parameter, we have minimized the objective function (Eq. 20) using PFP parameters derived from Eq. (21), for each pure component property. Table 11 presents the values of the parameters of each pure component at the corresponding temperature.

$$OF = \sum_i (h_{\text{exp},i}^E - h_{\text{PFP},i}^E)^2 \quad (20)$$

Table 11 Physical constants of pure compounds at different temperatures, used for calculations of excess molar volume V^E with PFP model: v_i^0 : molar volume, α_i coefficient of thermal expansion χ_T isothermal compressibility, reduction parameters of volume v_i^* , energy U_i^* and pressure p_i^* .

Compound	$v_i^0 / \text{cm}^3 \cdot \text{mol}^{-1}$	$10^3 \alpha_i / \text{K}^{-1}$	$10^3 \chi_T / \text{MPa}^{-1}$	$v_i^* / \text{cm}^3 \cdot \text{mol}^{-1}$	p_i^* / MPa	$U_i^* / \text{kJ} \cdot \text{mol}^{-1}$
$T = 313.15 \text{ K}$						
Furan	74.776	1.549	1.456	54.840	619.59	33.978
n-hexane	134.324	1.457	1.968	99.708	420.67	41.944
1-Octanol	160.540	0.865	0.851	130.660	480.51	62.783
$T = 353.15 \text{ K}$						
Furan	79.821	1.697	2.100	56.073	578.44	32.435
n-hexane	142.838	1.610	2.843	101.442	396.59	40.231
1-Octanol	166.358	0.917	1.074	131.496	482.76	63.482
$T = 383.15 \text{ K}$						
Furan	84.123	1.783	2.688	57.490	544.24	31.288
n-hexane	150.124	1.702	3.650	103.607	375.125	38.865
1-Octanol	171.078	0.951	1.273	132.448	477.61	63.258

The values of χ_{12} parameters are presented in Table 12 for the furan + n-hexane and for the furan + 1-octanol binary systems.

Table 12 χ_{12} parameters used in the PFP theory for binary systems

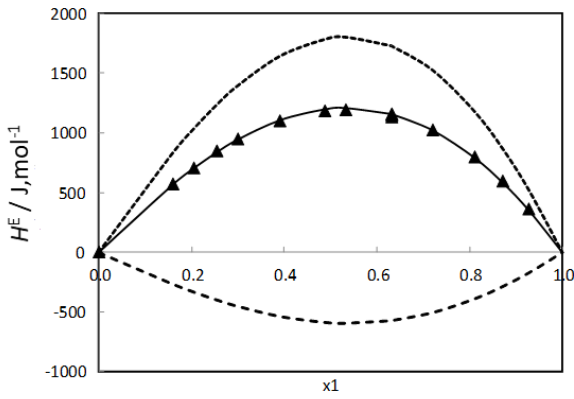
T / K	χ_{12}^0	a	b
furan + 1-octanol			
313.15	80.76	1.2595	0.9537

353.15	90.80	1.2747	0.8816
383.15	82.48	1.2220	0.7296
furan + n-hexane			
313.15	85.38	1.0654	0.4543
353.15	79.48	1.0747	0.4776
383.15	71.96	1.0407	0.4747

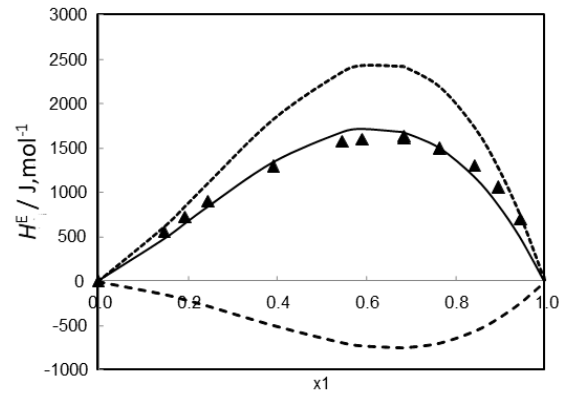
We have considered the same temperature dependency of the cross parameter χ_{12} (Eq.21) like in Coquelet *et al.* [20].

$$\chi_{12} = \chi_{12}^0(a + b(\phi_1 - \phi_2)) \quad (21)$$

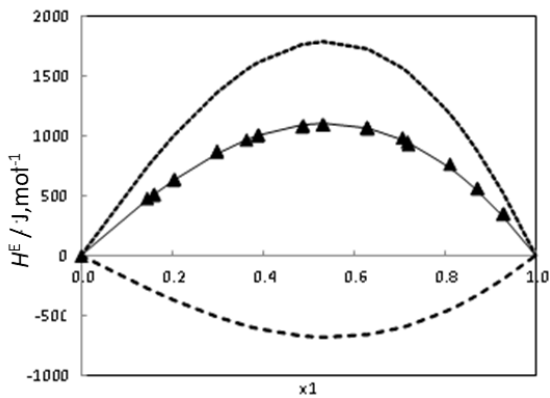
The χ_{12}^0 parameter expressed in Eq. (21) is determined by considering no composition dependency. a and b parameters are adjusted using objective function defined by Eq. (20) and taking χ_{12}^0 as a constant. The evolution of the contribution parameters with the temperature is shown in supplementary file.



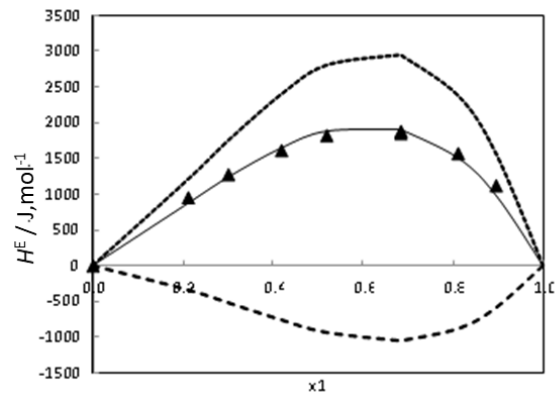
1A



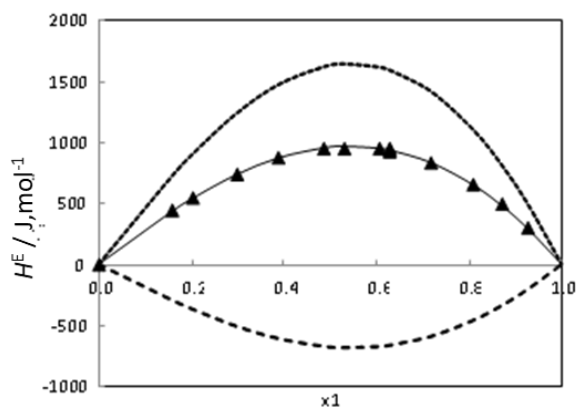
1B



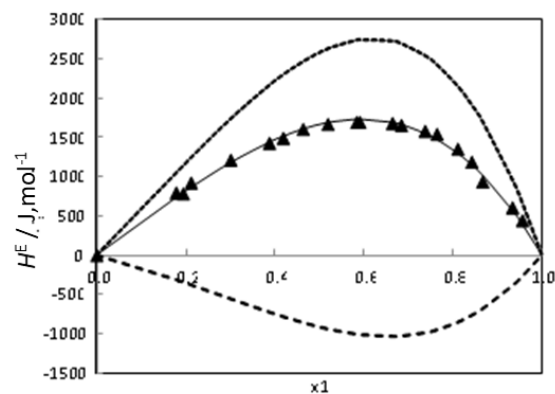
2A



2B



3A



3B

Fig. 6 Excess molar enthalpy at 313.15 K (1), 353.15 K (2) and 383.15 K (3) of furan + n-hexane (A) and furan + 1-octanol (B) binary systems as a function of molar composition. Solid line: PFP theory, dotted line: Interactional contribution, dashed line: free volume contribution.

The Fig. 6 shows the results obtained for each temperature for the two binary systems. The different contribution to the molar excess enthalpies is also indicated. The results are also presented in supplementary files. We can conclude that the interactional interactions are predominant and confirm the selection of NRTL activity coefficient model used to correlate the data.

For the two binary systems studied, and as it can be seen in Fig. 6 the main contribution to excess molar enthalpy is attributed to the interactional contribution. It highlights the importance of the χ_{12} parameter in the data treatment and the dependence to the composition of this parameter.

Conclusion

The experimental excess molar volume and enthalpy data for 3 binary mixtures containing furan have been presented at different temperatures and pressures, covering the entire composition range. The PFP model was used to correlate the data and identify the most predominant molecular interaction. The treatment confirms that the main molecular interactions are interactional type. Following the conclusion on our data treatment using PFP model, the selected NRTL activity coefficient model can be used to correlate experimental data. In order to understand the thermodynamic behaviour of oxygenated compounds, it could be of interest to represent the excess properties by a group contribution model. The thermodynamic model will make it possible to calculate the thermodynamic properties during the different steps of an industrial process such as manufacturing new products from the ligno-cellulosic material.

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