Available online at www.sciencedirect.com

Thermochimica Acta 441 (2006) 53–68

thermochimica acta

www.elsevier.com/locate/tca

Thermodynamics of organic mixtures containing amines
V. Systems with pyridines

Juan Antonio González*, Ismael Mozo, Isaías García de la Fuente, José Carlos Cobos

G.E.T.E.F. Dpto Termodinámica y Física Aplicada, Facultad de Ciencias, Universidad de Valladolid, Valladolid 47071, Spain

Received 13 July 2005; received in revised form 9 November 2005; accepted 15 November 2005
Available online 4 January 2006

Abstract

Binary mixtures containing pyridine (PY), or 2-methylpyridine (2MPY) or 3-methylpyridine (3MPY) or 4-methylpyridine (4MPY) and an organic solvent as benzene, toluene, alkane, or 1-alkanol are investigated in the framework of DISQUAC. The corresponding interaction parameters are reported. The model describes accurately a whole set of thermodynamic properties: vapor–liquid equilibria (VLE), liquid–liquid equilibria (LLE), solid–liquid equilibria (SLE), molar excess Gibbs energies (G^E), molar excess enthalpies, (H^E), molar excess heat capacities at constant pressure (C_P^E) and the concentration–concentration structure factor ($S_{CC}(0)$). It is remarkable that DISQUAC correctly predicts the W-shaped curve of the C_P^E of the pyridine + *n*-hexadecane system. The model can be applied successfully to mixtures with strong positive or negative deviations from the Raoult's law. DISQUAC improves the theoretical results from UNIFAC (Dortmund version). The replacement of pyridine by a methylpyridine leads to a weakening of the amine–amine interactions, ascribed to the steric effect caused by the methyl group attached to the aromatic ring. This explains that for a given solvent (alkane, 1-alkanol) $H^E(\text{pyridine}) > H^E(\text{methylpyridine})$.

Keywords: Thermodynamics; Pyridine; DISQUAC; Amine–amine interactions; Steric effect

1. Introduction

Amines are a very interesting class of compounds. Primary and secondary amines are weakly self-associated [1–8]. Note that their Trouton's constants (Table 1) are close to the value of non-associated species (92.05 J mol^{-1} K^{-1} [9]). For 1-alkanols, this constant is 110.88 J mol^{-1} K^{-1} [9]). Solutions of *N*,*N*,*N*-trialkylamines with aliphatic hydrocarbons, and particularly with homomorphic alkanes, are nearly ideal [10]. So, the investigation of mixtures with amines makes possible to examine the influence of some interesting effects on their thermodynamic properties, as well as to analyse the ability of any theoretical model to predict such properties. For example, linear amines ($CH_3(CH_2)_nNH_2$ or $CH_3(CH_2)_nN(CH_2)_m CH_3$) allow the study of the size and steric effects produced by alkylgroups attached to the amine group; *N*,*N*,*N*-trialkylamines, the effect of a globular shape; cyclic amines, the ring strain; aromatic amines, the effect of polarizability. Pyridine and its derivatives are examples of tertiary heterocyclic amines which are also useful to investigate the possible steric hindrance effect of the methyl groups. Moreover, the treatment of pyridine systems is a first step for a better understanding of the pyrrole ring, specially important to model typical binding sites on proteins [7].

Association of pyridine has been the subject of many studies in such way that different association mechanisms have been proposed. One of them assumes that the hydrogen bonds are formed between the ring nitrogen and the hydrogen at the α position to the N atom of the other molecule [11,12]. Alternately, the association of pyridine is considered as a result of *n*–π interactions between the free electron pair on the nitrogen of one molecule with the aromatic ring π electrons of another molecule [13,14]. The existence of pyridine dimers, which seems to be supported by neutron and X-ray scattering [15,16], has been also explained assuming that the N atom of a molecule and the H in γ position mutually interact with respect to the nitrogen in the ring of the other molecule.

On the other hand, different approaches have been applied to characterize mixtures containing pyridines, or to predict/correlate their thermodynamic properties. So, systems with alkanes or 1-butanol have been investigated in terms of the ERAS

---

* Corresponding author. Fax: +34 983 42 31 35.
E-mail address: jagl@termo.uva.es (J.A. González).

0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.11.027

Table 1
Physical constants[a] of pure amines

Amine	V (cm^3 mol^{-1})	T_b (K)	$\Delta_{vap}H$ (kJ mol^{-1})	$\Delta_{vap}H/T_b$ (kJ mol^{-1} K^{-1})	P_c (bar)	T_c (K)	μ (D)	$\bar{\mu}_{eff}$
Hexylamine	133.11[b]	405.9[c]	36.54[c]	90.02	33.1[d]	584[d]	1.38[e]	0.458
Dipropylamine	139.05[f]	382.4[c]	33.47[c]	87.53	31[f]	550[f]	1.02[f]	0.335
Triethylamine	94.28	362.1[c]	31.01[c]	85.64	30.4[f]	535.4[f]	0.87[f]	0.281
Cyclohexylamine	115.61[f]	407.1[c]	36.14[c]	88.77	42.6[d]	614.9[f]	1.26[f]	0.448
Aniline	91.53[f]	457.2[c]	42.44[c]	92.83	53.08[f]	699[f]	1.51[f]	0.604
Pyrrole	69.48[f]	403[c]	38.75[c]	96.15	57[f]	639.7[f]	1.8[f]	0.720
Pyridine (PY)	80.86[f]	388.4[c]	35.09[c]	90.34	60.8[f]	617.2[f]	2.37[f]	1.008
2-Methylpyridine (2MPY)	99.09[f]	402.6[c]	36.17[c]	89.84	46[f]	621.1[f]	1.97[f]	0.757
3-Methylpyridine (3MPY)	97.83[f]	417.3[c]	37.35[c]	89.50	44.8[f]	644.9[f]	2.4[f]	0.929
4-Methylpyridine (4MPY)	98.01[f]	418.5[c]	37.51[c]	89.63	46.6[f]	646.3[f]	2.6[f]	1.005

[a] V, molar volume at 298.15 K; T_b , boiling point; $\Delta_{vap}H$, standard enthalpy of vaporization at T_b; P_c, critical pressure; T_c, critical temperature; μ, dipole moment; $\bar{\mu}_{eff}$, effective dipole moment defined as: $[\mu^2 N_A/4\pi\varepsilon_0 V k_B T]^{1/2}$ [97]; N_A, Avogadro's number; ε_o, permittivity of vacuum; k_B, Boltzmann constant.

[b] [98].

[c] [88].

[d] estimated from Joback's method [99].

[e] [96].

[f] [89].

model [17,18] and aqueous solutions using the Kirkwood-Buff theory [19]. Unfortunaltely, ERAS does not represent the symmetry of the H^E curves of mixtures involving n-alkanes. The UNIQUAC equation was modified to predict accurately VLE data over a wide range of temperature [20]. In the framework of UNIFAC (Dortmund version [21]) interaction parameters for contacts between the pyridine group and other different group are available [22].

As continuation of our studies on mixtures containing amines [23–28], the first purpose of this article is to extend the purely physical model DISQUAC [29], based on the rigid lattice model developed by Guggenheim [30], to mixtures containing pyridines. The solvents considered are: benzene, toluene, alkanes and alkanols. Our second purpose is to gain insight into the interactions and structural effects present in solutions with pyridines. At this end, we analyse the experimental database and investigate the mixture structure in terms of the so-called concentration-concentration structure factor, $S_{CC}(0)$ [31]. We have shown elsewhere [28,32,33] that DISQUAC is a reliable tool to describe this important property.

2. Theory

2.1. DISQUAC

In the framework of DISQUAC, mixtures with pyridine or its methyl derivatives and an organic solvent are regarded as possessing the following four types of surface: (i) type n, N in the amine; (ii) type b, C_6H_5 in pyridine or C_6H_6 in benzene; (iii) type a, aliphatic (CH_3, CH_2, in n-alkanes, toluene, methylcyclohexane, alkanols); (iv) type s (s = c, c-CH_2 or c-CH in cycloalkanes; s = h, OH in 1-alkanols; s = p, C_6H_5 in toluene, or C_5H_4 in methylpyridines).

2.1.1. General equations

The main features of DISQUAC are: (i) The total molecular volumes, r_i, surfaces, q_i, and the molecular surface fractions, α_i, of the compounds present in the mixture are calculated additively on the basis of the group volumes R_G and surfaces Q_G recommended by Bondi [34]. As volume and surface units, the volume R_{CH_4} and surface Q_{CH_4} of methane are taken arbitrarily [35]. The geometrical parameters for the groups referred to in this work are listed in Table 2. (ii) The partition function is factorized into two terms, in such way that the excess functions are calculated as the sum of two contributions: a dispersive (DIS) term which represents the contribution from the dispersive forces; and a quasichemical (QUAC) term which arises from the anisotropy of the field forces created by the solution molecules. In the case of G^E, a combinatorial term, $G^{E,COMB}$, represented by the Flory-Huggins equation [35,36] must be considered. Thus,

$$G^E = G^{E,COMB} + G^{E,DIS} + G^{E,QUAC} \tag{1}$$

$$H^E = H^{E,DIS} + H^{E,QUAC} \tag{2}$$

(iii) The interaction parameters are assumed to be dependent on the molecular structure; (iv) The value $z = 4$ for the coordination number is used for all the polar contacts. This represents one of the more important shortcomings of the model, and is partially

Table 2
Geometrical parameters, volume, r_G , and surface, q_G, for the groups referred to in this work

Group	r_G	q_G	Ref.
CH_3	0.79848	0.73103	[35]
CH_2	0.59755	0.46552	[35]
c-CH_2	0.58645	0.66377–0.0385 m ($4 \le m \le 8$)	[100]
c-CH	0.38493	0.39480–0.0385 m ($4 \le m \le 8$)	[100]
C_6H_6	2.8248	2.0724	[35]
C_6H_{5-}	2.67752	1.83797	[35]
C_5H_{5-}	2.3540	1.7270	This work
C_5H_{4-}	2.2067	1.4925	This work
N (in aromatic ring)	0.25292	0.2000[a]	This work
OH	0.46963	0.50345	[37]

[a] Obtained together with the interchange coefficients from VLE and H^E data for the pyridine + benzene system.

removed via the hypothesis of considering structure dependent interaction parameters.

The equations used to calculate the DIS and QUAC contributions to G^E and H^E in the framework of DISQUAC are given elsewhere [37]. The temperature dependence of the interaction parameters is expressed in terms of the DIS and QUAC interchange coefficients [37], $C^{\mathrm{DIS}}_{\mathrm{st},l}$; $C^{\mathrm{QUAC}}_{\mathrm{st},l}$ where $s \neq$ t are two contact surfaces present in the mixture and $l = 1$ (Gibbs energy); $l = 2$ (enthalpy), $l = 3$ (heat capacity).

2.2. *Modified UNIFAC (Dortmund version)*

Modified UNIFAC [21] differs from the original UNIFAC [38] by the combinatorial term and the temperature dependence of the interaction parameters.

The equations to calculate G^E and H^E are obtained from the fundamental equation for the activity coefficient γ_i of component i:

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{COMB}} + \ln \gamma_i^{\mathrm{RES}} \tag{3}$$

where $\ln \gamma_i^{\mathrm{COMB}}$ is the combinatorial term and $\ln \gamma_i^{\mathrm{RES}}$ is the residual term. Equations are given elsewhere [23].

2.2.1. *Assessment of geometrical and interaction parameters*

In modified UNIFAC, a new main group "Pyridines", different to those of primary, secondary or tertiary alkylamines, is defined for the representation of the thermodynamic properties of pyridines + organic solvent mixtures. The main group is subdivided in three subgroups: AC2H2N, AC2HN, and AC2N [22]. Previously, pyridine was considered as homogeneous molecule [39]. The subgroups have different geometrical parameters, but the subgroups within the same main group are assumed to have identical interaction parameters. In UNIFAC, the geometrical parameters, the relative van der Waals volumes and the relative van der Waals surfaces are not calculated form molecular parameters like in the original UNIFAC but fitted together with the interaction parameters to the experimental values of the thermodynamic properties considered. The geometrical and interaction parameters were taken from literature and used without modifications [22,39].

2.3. *Concentration–concentration structure factor*

Mixture structure can be studied using the $S_{\mathrm{CC}}(0)$ function [31], defined as [31,40,41]:

$$S_{\mathrm{CC}}(0) = \frac{RT}{(\partial^2 G^{\mathrm{M}}/\partial x_1^2)_{P,T}} = \frac{x_1 x_2}{D} \tag{4}$$

with

$$D = \frac{x_1 x_2}{RT}\left(\frac{\partial^2 G^{\mathrm{M}}}{\partial x_1^2}\right)_{P,T} = 1 + \frac{x_1 x_2}{RT}\left(\frac{\partial^2 G^{\mathrm{E}}}{\partial x_1^2}\right)_{P,T} \tag{5}$$

D is a function closely related to thermodynamic stability [41,42]. For ideal mixtures, $G^{\mathrm{E,id}} = 0$; $D_{\mathrm{id}} = 1$ and $S_{\mathrm{CC}}(0) = x_1 x_2$. As stability conditions require, $S_{\mathrm{CC}}(0) > 0$, and if the system is close to phase separation, $S_{\mathrm{CC}}(0)$ must be large and positive (∞, when the mixture presents a miscibility gap). In contrast, if compound formation between components appears, $S_{\mathrm{CC}}(0)$ must be very low (0, in the limit). So, if $S_{\mathrm{CC}}(0) > x_1 x_2$, i.e., $D < 1$, the dominant trend in the system is the separation of the components (homocoordination), and the mixture is less stable than the ideal. If $0 < S_{\mathrm{CC}}(0) < x_1 x_2 = S_{\mathrm{CC}}(0)^{\mathrm{id}}$, i.e., $D > 1$, the fluctuations in the system have been removed, and the dominant trend in the solution is compound formation (heterocoordination). In this case, the system is more stable than ideal.

3. Estimation of the model parameters

3.1. *Disquac interaction parameters*

The general procedure applied in the estimation of the interaction parameters has been explained in detail elsewhere [43]. Final values of the fitted parameters in this work are collected in Table 3. Some important remarks are given below.

3.1.1. *Pyridine + benzene system*

This mixture is characterized by the contact (b, n), which is assumed to be represented by DIS parameters only. This choice is reasonable if one takes into account: (a) the low H^E(8 J mol^{-1} at equimolar composition and 298.15 K [44]); (b) the SLE phase diagram shows a single eutectic point with no evidence for compound formation in the solid state [45]; (c) $(\partial V^E/\partial T)_p$ is negative and suggests that complex formation is not the major contribution to the negative V^E [46]; (d) C_P^E is slightly positive [44], a characteristic of systems where dipolar or dipole-induced dipole interactions are present [47]. Nevertheless, it should be pointed out that the H^E curve is skewed towards low mole fraction of pyridine [44], which has been interpreted in terms of specific interactions between unlike molecules [48]. In addition NMR measurements were developed to infer the possible geometry of the complex [49].

3.1.2. *Pyridine + n-alkane, or + cyclohexane systems*

The mixtures with n-alkanes are built by three contacts: (a, b), (b, n) and (a, n). The (a, b) contacts are represented by DIS parameters only, which are known from experimental data of benzene + n-alkane systems [50]. The $C^{\mathrm{DIS}}_{\mathrm{ab},l}$ coefficients change regularly with the n-alkane due to the so-called Patterson effect, a positive enthalpic contribution which appears when longer chain n-alkanes are mixed with globular molecules. This is attributed to the order-destruction of the longer n-alkanes during the mixing process [51,52]. As the parameters for the (a, b) and (b, n) contacts are then known (see above), only the interchange coefficients for the (a, n) contacts must be now fitted. This is somewhat difficult because pyridine + n-alkane systems show miscibility gaps at low temperatures [53]. DISQUAC is a mean field theory and LLE calculations are developed under the basic and wrong assumption that G^E is an analytical function close to the critical point. The instability of a system is given by $(\partial^2 G^{\mathrm{M}}/\partial x_1^2)_{P,T}$ ($G^{\mathrm{M}} = G^{\mathrm{E}} + G^{\mathrm{ideal}}$) and represented by the critical exponent $\gamma > 1$ in the critical exponents theory [42]. According to this theory,

Table 3
Dispersive (DIS) and quasichemical (QUAC) interchange coefficients ($l = 1$, Gibbs energy; $l = 2$, enthalpy, $l = 3$, heat capacity) for (s, n) contacts in mixtures containing pyridines

System[a]	Contact (s, n)[b]	$C^{\mathrm{DIS}}_{\mathrm{sn},1}$	$C^{\mathrm{DIS}}_{\mathrm{sn},2}$	$C^{\mathrm{DIS}}_{\mathrm{sn},3}$	$C^{\mathrm{QUAC}}_{\mathrm{sn},1}$	$C^{\mathrm{QUAC}}_{\mathrm{sn},2}$	$C^{\mathrm{QUAC}}_{\mathrm{sn},3}$
PY + $CH_3(CH_2)_nCH_3$ ($n \leq 5$)	(a, n)	8.8	1	22.2	7	14.1	−20
PY + $CH_3(CH_2)_6CH_3$	(a, n)	8.6	1	22.5	7	14.1	−20
PY + $CH_3(CH_2)_7CH_3$	(a, n)	8.5	1	22.7	7	14.1	−20
PY + $CH_3(CH_2)_8CH_3$	(a, n)	8.4	1	23	7	14.1	−20
PY + $CH_3(CH_2)_{10}CH_3$	(a, n)	8.1	1	23.4	7	14.1	−20
PY + $CH_3(CH_2)_nCH_3$ ($n \geq 10$)	(a, n)	7.9	1	23.7	7	14.1	−20
PY + C_6H_{12}	(c, n)	8.6	1.1	21.8	7	14.1	−20
PY + benzene	(b, n)	9.5	0.65	24			
PY + toluene	(p, n)	11	0.65	24			
2MPY + *n*-alkane	(a, n)	9.05	10	26	7	12	−20
2MPY + C_6H_{12}	(c, n)	9.05	10.7	26	7	12	−20
2MPY + benzene, or +toluene	(s, n)[c]	10.45	9.1	23			
3MPY or 4MPY + *n*-alkane	(a, n)	14.4	10	26	7	12	−20
3MPY or 4MPY + C_6H_{12}	(c, n)	14.4	10.7	26	7	12	−20
3MPY or 4MPY + benzene, or +toluene	(s, n)[c]	14.9	8.4	23			
PY + methanol	(h, n)	−11.1	−22.8	10	−3.9	−1.9	−5
PY + ethanol	(h, n)	−11.4	−22.8	10	−3.5	0.15	−5
PY + 1-propanol	(h, n)	−16	−29	10	−3.5	0.15	−5
PY + ≥1-butanol	(h, n)	−17.6	−29	10	−3.5	0.15	−5
2MPY + methanol	(h, n)	−15.1	−35.5	10	−3.9	−1	−5
2MPY + ethanol	(h, n)	−13.9	−35.5	10	−3.5	2	−5
2MPY + 1-propanol	(h, n)	−18.5	−35.5	10	−3.5	2	−5
2MPY + ≥1-butanol	(h, n)	−20.5	−35.5	10	−3.5	2	−5
3MPY or 4MPY + methanol	(h, n)	−11	−35.5	10	−3.9	−1	−5
3MPY or 4MPY + ethanol	(h, n)	−12	−35.5	10	−3.5	0.35	−5
3MPY or 4MPY + 1-propanol	(h, n)	−17.2	−35.5	10	−3.5	0.35	−5
3MPY or 4MPY + ≥1-butanol	(h, n)	−20.	−35.5	10	−3.5	0.35	−5

[a] For symbols, see Table 1.

[b] *s* = a, CH_3 or CH_2 in *n*-alkanes, methylcyclohexane, toluene, 1-alkanols, or methylpyridines; s = b, C_6H_6 or C_6H_5 in pyridine; s = c, c-CH_2 in cyclohexane or methylcyclohexane; c-CH in methylcyclohexane; s = h, OH in 1-alkanols; s = p, C_6H_5 in toluene or C_6H_4 in methylpyridine; s = n, N in pyridines.

[c] *s* = b, p.

mean field models ($\gamma = 1$) provide LLE curves which are too high at the UCST (upper critical solution temperature) and too low at the LCST [42] (lower critical solution temperature). Thus, one must keep the $C^{\mathrm{DIS/QUAC}}_{\mathrm{an},1}$ coefficients between certain limits in order to provide not very high calculated UCSTs. The same occurs, e.g., for sulfolane [43], alkoxyethanol [54], crown ether [55], or amide [32,33,47] + alkane mixtures.

The pyridine + cyclohexane system is formed by the contacts: (b, c); (b, n) and (c, n). For the (b, c) contacts, the interchange coefficients are $C^{\mathrm{DIS}}_{\mathrm{bc},1} = 0.2445$ and $C^{\mathrm{DIS}}_{\mathrm{bc},1} = 0.5619$ [35]. The interaction parameters for the (b,n) contacts are known, so only the $C^{\mathrm{DIS/QUAC}}_{\mathrm{cn},l}$ coefficients must be determined. Calculations were carried out assuming that $C^{\mathrm{QUAC}}_{\mathrm{an},l} = C^{\mathrm{QUAC}}_{\mathrm{cn},l}$. This general rule is valid for many other solutions as sulfolane [43], alkoxyethanol [54], amide [32,33,47], linear oxaalkane, linear alkanone, linear organic carbonate, alkanoic acid anhydride, chloroalkane, linear carboxylic acid, alkanol, or aniline + *n*-alkane, or +cyclohexane mixtures (see [28] and references herein).

Table 4
Upper critical solution points, temperatures, T_c, and compositions, x_{1c}, for pyridine(1) + *n*-alkane(2) mixtures calculated using DISQUAC (DQ) with interaction parameters from Table 3

n-Alkane	T_c (K)		x_{1c}		Ref.
	Exp.	DQ.	Exp.	DQ.	
n-C_6	252.2	253.6	0.413	0.584	[53]
n-C_7	255.2	260.6	0.441	0.634	[53]
n-C_8		262.3		0.678	
n-C_9		266.1		0.708	
n-C_{10}		269.8		0.742	
n-C_{12}	268.7	272.5	0.652	0.787	[53]

Comparison with experimental (exp.) values.

3.1.3. Pyridine + toluene system

In order to reduce the number of interaction parameters, no distinction was made between the aromatic ring in pyridine and toluene. The mixture is then characterized by three contacts: (a, p); (a, n) and (p, n). Similar considerations to those stated for the interaction parameters of the (a, b) contacts remain valid for those of the (a, p) contacts [50]. Therefore, we must only fit $C^{\mathrm{DIS/QUAC}}_{\mathrm{np},l}$ coefficients. This was done assuming that the parameters are dispersive only. In previous studies, we have found that mixtures with benzene or toluene differ in the DIS parameters. This is the case of systems involving 1-alkanol [56,57], 2-alkanol [58], sulfolane [43] or amide [32,33,47].

Table 5
Molar excess Gibbs energies, G^E, at equimolar composition and temperature T, for pyridine(1) or methylpyridine(1) + organic solvent(2) mixtures

Solvent	T (K)	N[a]	G^E (J mol^{-1})			σ_r (P)[b]			Ref.
			Exp[c]	DQ.[d]	UNIF.[e]	Exp.[c]	DQ.[d]	UNIF.[e]	
Pyridine(1) + organic solvent(2)									
Benzene	298.15	8	125	125	140	0.001	0.004	0.011	[101]
			127						[46]
	323.15		132	133	150	0.005	0.006		[101]
Toluene	298.15	10	225	220	249	0.005	0.015		[101]
		11					0.013	0.021	[102]
	333.15		220	222	262				[101]
	373.15	12	213	218	266	0.0002	0.003	0.014	[103]
Hexane	298.15	10	1074	1076	1099	0.011	0.017	0.019	[104]
	328.15	10	1020	1022	1062	0.011	0.015	0.023	[104]
	338.15		927	986	1053				[68]
Heptane	298.15	9	1071	1085	1053	0.004	0.012	0.010	[104]
	313.15	16	1033	1053	1024	0.001	0.016	0.008	[105]
	333.15	9	991	1011	994	0.004	0.010	0.004	[104]
	340.95		968	996	984	0.003	0.012	0.008	[106]
	348.15		985	982	976				[68]
	353.15	12	910	972	970	0.001	0.012	0.013	[106]
Octane	313.15	12	1020	1022	977	0.003	0.008	0.018	[105]
	348.15		932	936	915				[68]
	353.15	14	889	925	908	0.003	0.020	0.013	[106]
	369.75	11	824	890	880	0.003	0.025	0.023	[106]
Nonane	313.15	16	1008	1002	935	0.003	0.009	0.033	[105]
	348.15		941	904	861				[68]
	353.15	15	857	891	852	0.008	0.021	0.011	[106]
	369.75	12	839	851	820	0.004	0.008	0.013	[106]
Decane	348.15		569	867	812				[68]
	353.15	10	839	854	802	0.003	0.036	0.016	[106]
	373.15	9	772	799	758	0.013	0.040	0.029	[106]
C_6H_{12}	293.15	12	925	926	939	0.003	0.007	0.014	[102]
	298.15	12	918	918	933	0.004	0.009	0.018	[102]
	313.15	12	888	892	912	0.002	0.008	0.026	[102]
Methanol	298.15	10	−100	−98	−177	0.005	0.012	0.033	[90]
	303.15	10	−225	−88	−169	0.003	0.064	0.027	[107]
	308.15	10	−78	−78	−160	0.003	0.012	0.033	[90]
	313.15	13	−74	−69	−150	0.001	0.011	0.028	[108]
	318.15	10	−60	−61	−138	0.001	0.011	0.031	[90]
	373.2	5	34	1	89	0.012	0.023	0.024	[109]
Ethanol	313.15	15	−1.5	6	−143	0.0004	0.003	0.042	[108]
	338.15	22	29	3	−108	0.002	0.008	0.036	[110]
	348.15	23	38	−2	−88	0.005	0.012	0.032	[110]
1-Propanol	313.15	15	−113	−107	−240	0.0004	0.006	0.032	[108]
	343.15	23	−107	−126	−217	0.0009	0.007	0.022	[110]
	363.15	28	−108	−137	−180	0.003	0.011	0.016	[110]
1-Butanol	313.15	14	−135	−112	−310	0.004	0.015	0.056	[108]
	343.15	24	−78	−150	−306	0.001	0.023	0.057	[110]
	363.15	24	−107	−171	−278	0.001	0.018	0.039	[110]
2-Methylpyridine(1) + organic solvent(2)									
Benzene	313.15	14	57	59	22	0.002	0.004	0.017	[105]
Toluene	313.15	16	114	101	54	0.002	0.007	0.021	[105]
	373.15	12	101	98	44	0.0002	0.001	0.015	[111]
Hexane	338.15		711	732	602				[68]
Heptane	313.15	16	770	783	572	0.002	0.007	0.080	[105]
	348.15		714	722	541				[68]
Octane	313.15	16	771	791	532	0.002	0.011	0.079	[105]

Table 5 (*Continued*)

Solvent	T (K)	N[a]	G^E (J mol^{-1}) Exp[c]	DQ.[d]	UNIF.[e]	σ_r (P)[b] Exp.[c]	DQ.[d]	UNIF.[e]	Ref.
	348.15		754	722	491				[68]
Nonane	313.15	15	769	791	496	0.004	0.017	0.094	[105]
	348.15		733	714	446				[68]
Decane	348.15		303	705	405				[68]
Methanol	298.15	10	−249	−246	214	0.002	0.023	0.250	[112]
	308.15			−213	237				[112]
	313.15	17	−193	−197	249	0.005	0.024	0.23	[108]
	318.15	10	−171	−181	262	0.001	0.022	0.220	[112]
Ethanol	313.15	14	−100	−102	91	0.002	0.005	0.081	[108]
1-Propanol	313.15	14	−234	−237	−43	0.0005	0.007	0.071	[108]
1-Butanol	313.15	16	−274	−269	−144	0.002	0.012	0.044	[108]
3-Methylpyridine(1) + organic solvent(2)									
Benzene	313.15	16	65	72	−116	0.002	0.005	0.085	[105]
Toluene	313.15	16	137	148	−6	0.003	0.010	0.052	[105]
	373.15	11	148	156	82	0.0008	0.005	0.014	[113]
Methanol	313.15	13	−129	−155	−193	0.010	0.033	0.032	[114]
Ethanol	313.15	13	−57	−95	−214	0.001	0.018	0.065	[114]
1-Propanol	313.15	15	−176	−221	−355	0.004	0.015	0.056	[114]
1-Butanol	313.15	13	−226	−251	−457	0.002	0.012	0.056	[114]
4-Methylpyridine(1) + organic solvent(2)									
Benzene	313.15	15	77	72	−116	0.004	0.004	0.094	[105]
Toluene	313.15	16	156	148	−6	0.001	0.009	0.058	[105]
Methanol	313.15	14	−201	−155	−193	0.004	0.034	0.024	[114]
Ethanol	313.15	15	−112	−95	−214	0.002	0.009	0.046	[114]
1-Propanol	313.15	17	−234	−221	−355	0.002	0.011	0.043	[114]
1-Butanol	313.15	16	−266	−251	−457	0.003	0.017	0.049	[114]

[a] Number of data points.
[b] Eq. (6).
[c] Experimental result.
[d] DISQUAC values calculated with interaction parameters from Table 3.
[e] UNIFAC values calculated with interaction parameters from the literature [22,39].

Table 6
Coordinates of azeotropes, temperature, T_{az}, mole fraction, x_{1az}, and pressure, P_{az}, for pyridine(1) or 2-methylpyridine(1) + organic solvent mixtures(2)

System[a]	T_{az} (K)	x_{1az} Exp[b].	DQ[c]	P_{az} (kPa) Exp[b].	DQ[c]	Ref.
PY + C_7H_8	298.15	0.1346	0.092	3.883	3.794	[101]
		0.118		3.851		[102]
PY + n-C_7	298.15	0.2676	0.274	6.873	6.898	[104]
	313.15	0.911	0.903	6.18	6.221	[105]
	353.15	0.283	0.304	62.2	62.75	[106]
PY + n-C_8	313.15	0.648	0.662	7.69	7.74	[105]
	369.75	0.665	0.676	67.06	68.91	[106]
PY + n-C_9	369.75	0.925	0.914	58.18	58.55	[106]
PY + C_6H_{12}	313.15	0.039	0.038	24.73	24.71	[102]
2MPY + n-C_8	313.15	0.452	0.434	5.08	5.13	[105]
2MPY + n-C_9	313.15	0.858	0.851	3.56	3.57	[105]

[a] For symbols, see Table 1.
[b] Experimental value.
[c] DISQUAC results calculated with the interaction parameters from Table 3.

3.1.4. Methylpyridine +benzene, +toluene, or +n-alkane systems

We have now three contacts: (a, p); (a, n) and (p, n). To determine the interaction parameters, the following restrictions were applied:

Table 7
Solid–liquid equilibria[a] for pyridine(1) or 2-methyl pyridine(1) + organic solvent(2) mixtures

System[b]	x_{1eu} Exp[d].	DQ.[e]	T_{eu} (K) Exp.[d]	DQ.[e]	Δ[c] (K)	Ref.
PY + benzene	0.715	0.752	216.05	212.94	2.5	45
2MPY + n-C_6	0.032	0.027	171.35	177.8	0.8	115
2MPY + n-C_7	0.095	0.039	181.3	182.12	2.4	115
2MPY + n-C_8	0.056	0.069	202.99	204.24	0.33	115
2MPY + n-C_{16}					1.2	115

[a] Coordinates of the eutectic point: composition, x_{1eu}, and temperature, T_{eu}.
[b] For symbols, see Table 1.
[c] $\Delta = \sum |T_{exp} - T_{calc}/N|$.
[d] Experimental value.
[e] DISQUAC results calculated with the interaction parameters from Table 3.

Table 8
Molar excess enthalpies, H^E, at equimolar composition and temperature T, for pyridine(1) or methylpyridine(1) + organic solvent(2) mixtures

Solvent	T (K)	N[a]	H^E (J mol^{-1})			dev (H^E)[b]			Ref.
			Exp[c]	DQ.[d]	UNIF.[e]	Exp[c]	DQ.[d]	UNIF.[e]	
Pyridine(1) + organic solvent(2)									
Benzene	279.15		−22	−12	−15				[116]
	288.15		−5	−2	−8				[48]
			−12						[116]
	298.15		8	9	3				[117]
			8			0.057	0.287	0.950	[48]
			8						[118]
			0						[116]
			−0.7						[119]
	303.15		8	14	9				[120]
	313.15		24	25	23				[48]
	333.15	11	44	46	45	0.036	0.161	0.341	[48]
Toluene	283.15		144	157	133				[116]
	298.15	7	171	183	124	0.021	0.117	0.240	[116]
		14	190			0.050	0.147	0.289	[121]
	308.15	14	226	199	126	0.004	0.208	0.429	[122]
	318.15	15	221	213	137	0.045	0.117	0.303	[121]
Hexane	298.15	20	1605	1611	1561	0.0008	0.005	0.052	[80]
		10	1541			0.040	0.071	0.084	[17]
	313.15	12	1609	1618	1469	0.008	0.040	0.066	[123]
Heptane	298.15	20	1735	1717	1687	0.0009	0.011	0.041	[80]
		24	1729			0.003	0.027	0.046	[17]
	313.15	14	1771	1723	1578	0.007	0.018	0.097	[123]
Octane	298.15	20	1801	1819	1801	0.001	0.031	0.025	[80]
		21	1756			0.003	0.039	0.031	[17]
	313.15	18	1961	1826	1675	0.004	0.039	0.104	[123]
Nonane	298.15	19	1843	1913	1904	0.008	0.037	0.030	[17]
	313.15	17	2184	1918	1762	0.003	0.096	0.162	[123]
Decane	298.15	20	1963	2006	1999	0.001	0.025	0.021	[80]
		19	1945			0.002	0.031	0.024	[17]
Dodecane	298.15	20	2140	2178	2239	0.001	0.033	0.034	[80]
Hexadecane	298.15	20	2349	2491	2432	0.002	0.064	0.028	[80]
C_6H_{12}	283.15		1452	1356	1200				[124]
	288.15	19	1318	1378	1229	0.07	0.036	0.145	[102]
	298.15	14	1438	1416	1295	0.007	0.018	0.128	[119]
		14	1400			0.004	0.029	0.168	[125]
		19	1348			0.011	0.056	0.168	[102]
		8	1415			0.019	0.029	0.158	[120]
		8	1429			0.022	0.033	0.155	[124]
	303.15	18	1481	1431	1333	0.019	0.081	0.221	[102]
	308.15	14	1380	1445	1373	0.004	0.053	0.137	[125]
	318.05	15	1533	1465	1457	0.004	0.030	0.089	[126]
$CH_3C_6H_{11}$	298.15	10	1505	1533		0.009	0.026		[124]
Methanol	298.15	38	−711	−714	−606	0.006	0.022	0.105	[93]
	303.15		−840	−692	−679				[127]
			−297						[63]
	308.15		−800	−667	−757				[127]
Ethanol	298.5		−162	−169	−377				[110]
	303.15		−69	−132	−402				[63]
1-Propanol	298.15		−4	−40	−165				[110]
	303.15		−36	−12	−202				[63]
1-Butanol	298.15	16	182	183	34	0.013	0.126	0.714	[18]
			188						[110]
	303.15		−366	208	−11				[64]
1-Hexanol	303.15	12	439	438	312	0.011	0.039	0.339	[128]
1-Heptanol	293.15	16	511	507	561	0.035	0.067	0.226	[129]

Table 8 (*Continued*)

Solvent	T (K)	N[a]	H^E (J mol^{-1})			dev (H^E)[b]			Ref.
			Exp[c]	DQ.[d]	UNIF.[e]	Exp[c]	DQ.[d]	UNIF.[e]	
	303.15	14	630	543	445	0.035	0.092	0.401	[129]
1-Octanol	293.15	14	688	660	690	0.028	0.090	0.141	[129]
	303.15	14	737	694	561	0.035	0.110	0.266	[129]
2-methylpyridine(1) + organic solvent(2)									
Benzene	283.15		28	37	−33				[116]
	298.15		39	32	−18				[117]
		11	33			0.025	0.142	1.33	[44]
			33						[130]
			29						[116]
			25						[119]
	308.15		117	31	−1				[122]
	313.15	7	29	31	9	0.025	0.217	0.690	[44]
Toluene	283.15		56	71	−25				[116]
	298.15		75	82	−16				[130]
		7	78			0.046	0.102	1.02	[116]
Hexane	298.15	22	1025	1235	968	0.004	0.195	0.086	[131]
		19	1218			0.018	0.029	0.162	[94]
Heptane	298.15	20	1212	1324	1047	0.002	0.107	0.143	[131]
		11	1346			0.014	0.020	0.187	[94]
Octane	298.15	21	1271	1406	1120	0.002	0.107	0.112	[131]
		10	1405			0.015	0.018	0.166	[94]
Nonane	298.15	21	1328	1484	1186	0.004	0.113	0.099	[131]
Decane	298.15	23	1412	1556	1246	0.001	0.106	0.100	[131]
		9	1486			0.016	0.052	0.127	[94]
Dodecane	298.15	16	1602	1688	1401	0.011	0.056	0.103	[94]
Hexadecane	298.15	8	1772	1912	1527	0.011	0.073	0.129	[94]
C_6H_{12}	283.15		1259	1231	817				[124]
	298.15	13	1180	1278	852	0.006	0.069	0.218	[119]
		9	1240			0.018	0.027	0.224	[124]
		22	1256			0.017	0.025	0.226	[130]
		10	1250			0.014	0.031	0.198	[120]
$CH_3C_6H_{11}$	283.15		1190	1139		0.011	0.037		[124]
	298.15		1170	1173					[124]
methanol	293.15	12	−1224	−1272	−419	0.030	0.069	0.541	[132]
	298.15	30	−1261	−1254	−442		0.028	0.517	[93]
1-propanol	313.15		30	−166	−214				[66]
1-hexanol	303.15		247	221	−3				[128]
3-Methylpyridine(1) + organic solvent(2)									
Benzene	298.15		10	1.4	−465				[117]
			1						[44]
			−4						[119]
	313.15		3.6	0.6	−535				[44]
Hexane	298.15	28	1125	1297	1402	0.004	0.151	0.196	[133]
		17	1278			0.003	0.012	0.055	[134]
Heptane	298.15	29	1344	1389	−1507	0.002	0.068	0.098	[133]
		17	1371			0.001	0.009	0.058	[134]
Octane	298.15	27	1443	1474	1600	0.003	0.053	0.082	[133]
		17	1400			0.002	0.033	0.085	[134]
Nonane	298.15	29	1503	1555	1683	0.003	0.049	0.090	[133]
Decane	298.15	28	1570	1629	1758	0.003	0.042	0.082	[133]
		17	1575			0.001	0.026	0.077	[134]
Dodecane	298.15	17	1673	1764	1944	0.002	0.042	0.117	[134]
Hexadecane	298.15	17	1905	1994	2089	0.005	0.045	0.085	[134]

Table 8 (*Continued*)

Solvent	T (K)	N[a]	H^E (J mol^{-1})			dev (H^E)[b]			Ref.
			Exp[c]	DQ.[d]	UNIF.[e]	Exp[c]	DQ.[d]	UNIF.[e]	
C_6H_{12}	298.15	12	1308	1333	1485	0.008	0.029	0.160	[119]
		12	1320			0.004	0.033	0.148	[125]
		9	1326			0.009	0.015	0.155	[120]
	308.15	12	1320	1355	1561	0.004	0.076	0.213	[125]
$CH_3C_6H_{11}$	298.15		1313						[120]
Methanol	293.15		−919	−1236	−615				[65]
	303.15	14	−1191	−1196	−861	0.004	0.151	0.186	[127]
			−780						[65]
	308.15		−1089	−1170	−994				[127]
Ethanol	303.15		438	−688	−519				[65]
1-Propanol	293.15		−228	−467	−287				[65]
	303.15		−216	−406	−334				[65]
	313.15		−238	−341	−403				[66]
1-Butanol	303.15		−98	−188	−160				[65]
	313.15		−95	−130	−259				[66]
	323.15		−54	−74	−367				[66]
1-Hexanol	293.15		−26	7	236				[66]
	303.15		−62	54	123				[128]
	313.15		55	98	−24				[66]
4-methylpyridine(1) + organic solvent(2)									
Benzene	298.15		18	1.4	−465				[117]
			9						[119]
Hexane	298.15	17	1302	1297	1402	0.001	0.027	0.046	[134]
		23	1161			0.005	0.120	0.171	[135]
Heptane	298.15	17	1407	1388	1507	0.001	0.018	0.040	[134]
		21	1384			0.004	0.079	0.092	[135]
Octane	298.15	17	1483	1474	1600	0.001	0.009	0.046	[134]
		24	1549			0.010	0.050	0.076	[135]
Nonane	298.15	22	1547	1555	1683	0.002	0.037	0.067	[135]
Decane	298.15	17	1617	1629	1758	0.002	0.006	0.057	[134]
		22	1602			0.003	0.044	0.076	[135]
Dodecane	298.15	17	1712	1764	1944	0.002	0.022	0.099	[135]
Hexadecane	298.15	17	1966	1994	2089	0.004	0.022	0.065	[135]
C_6H_{12}	298.15	15	1365	1333	1485	0.008	0.018	0.127	[119]
Methanol	293.15		−769	−1236	−615				[132]
	303.15		−684	−1196	−861				[132]
1-Hexanol	303.15		4	54	123				[128]

[a] Number of data points.

[b] Eq. (7).

[c] Experimental result.

[d] DISQUAC values calculated with interaction parameters from Table 3.

[e] UNIFAC values calculated with interaction parameters from the literature [22,39].

Systems with 3MPY or 4MPY are characterized by the same interchange coefficients. This is supported by the fact that 2MPY shows lower values of T_b(boiling temperature), $\Delta_{vap}H$ (standard enthalpy of vaporization) and $\bar{\mu}_{eff}$ (effective dipole moment) than the other methylpyridines (Table 1). It has been pointed out that interactions between molecules of 2MPY are weaker than those between molecules of 3MPY or 4MPY [12,59,60]. As a matter of fact, excess functions for water + 3MPY, or +4MPY [59] are essentially the same.

Mixtures with benzene or toluene are characterized by the same interaction parameters, i.e., the aromatic rings in benzene and methylpyridines are represented by the same contact surface.

3.1.5. *Methylpyridine + cyclohexane system*

Here, we have six types of contacts: (a, c); (a, p), (a, n), (c, p); (n, p,) and (c, n). In the calculations, we used $C^{DIS}_{ac,1} = 0.065$; $C^{DIS}_{ac,2} = 0.115$; $C^{DIS}_{ac,3} = -0.188$ [36], and$C^{DIS}_{cp,1} = 0.33$; $C^{DIS}_{cp,2} = 0.65$ [61]. The interaction parameters for the (a, p), (a, n) and (n, p) are kown, those for the (c, n) contacts were fitted newly under the basic assumption that $C^{QUAC}_{an,l} = C^{QUAC}_{cn,l}$.

Table 9
Molar partial excess enthalpies at 298.15 K and infinite dilution, $H_i^{E,\infty}$, for pyridine(1) or methylpyridine(1) + n-alkane(2) mixtures

System[a]	$H_1^{E,\infty}$/kJ mol^{-1}			$H_2^{E,\infty}$/kJ mol^{-1}		
	Exp.[b]	DQ.[c]	UNIF.[d]	Exp.[b]	DQ.[c]	UNIF.[d]
PY + n-C_7[e]	8.74	9.60	8.50	7.65	7.73	6.08
PY + n-C_{10}[e]	9.01	9.62	8.50	10.10	10.62	8.37
PY + n-C_{16}[e]	8.95	9.82	8.50	15.60	17.20	12.93
3MPY + n-C_7[f]	7.03 (7.46)[g]	6.83	6.51	5.98 (6.16)[g]	6.26	5.29
3MPY + n-C_{10}[f]	7.22 (7.56)[g]	7.89	6.51	7.90 (8.12)[g]	7.81	7.27
3MPY + n-C_{16}[f]	7.36 (7.76)[g]	7.95	6.51	11.80 (12.20)[g]	12.22	11.25

[a] For symbols, see Table 1.
[b] Experimental result.
[c] DISQUAC values calculated with interaction parameters from Table 3.
[d] UNIFAC values calculated with interaction parameters from the literature [22,39].
[e] [80].
[f] [134].
[g] Value for system with 4MPY [134].

3.1.6. Amine + 1-alkanol systems

These systems are characterized by the following contacts: (a, s); (a, n); (a, h); (n, s); (s, h) and (h, n), where s = b (in pyridine mixtures) and s = p (in methylpyridine solutions). The (a, h) contacts in 1-alkanol + n-alkane mixtures are described by DIS and QUAC interaction parameters [37,62]. Similarly it occurs for the (s, h) contacts in 1-alkanol + benzene, or +toluene systems [56,57]. We also assumed that the $C_{\text{hn},l}^{\text{DIS/QUAC}}$ coefficients are the same for mixtures containing 3MPY or 4MPY.

4. Results

Results from the DISQUAC model are compared with experimental data for LLE, VLE, G^E, SLE, H^E, $H_i^{E,\infty}$(molar partial excess enthalpy at infinite dilution), C_P^E and $S_{CC}(0)$ in Tables 4–11. Comparisons for selected mixtures are plotted in Figs. 1–7. For the sake of clarity, relative deviations for the pressure (P) and H^E defined as:

$$\sigma_r(P) = \left\{ \frac{1}{N} \sum \left[\frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{exp}}} \right]^2 \right\}^{1/2} \tag{6}$$

and

$$\text{dev}(H^E) = \left\{ \frac{1}{N} \sum \left[\frac{H_{\text{exp}}^E - H_{\text{calc}}^E}{|H_{\text{exp}}^E(x_1 = 0.5)|} \right]^2 \right\}^{1/2} \tag{7}$$

are given in Tables 5 and 8, where N stands for the number of data points for each system. In view of these results, it is possible to conclude that DISQUAC represents consistently the thermodynamic properties of the systems under study. Large deviations between measured and calculated values merely underline the existence of experimental inaccuracies [63–68] (e.g., see results in Table 8 at 303.15 K for pyridine + methanol or +1-butanol, or for 2- or 3-methylpyridine + 1-propanol). This remarks that the database must be critically reviewed previously to the fitting of the interaction parameters, a characteristic procedure when using DISQUAC. The theoretical results for LLE, VLE and SLE indicate that DISQUAC can be applied over a wide range of temperature. The coordinates of the critical points of pyridine + n-alkane mixtures are represented in the correct range of temperature and composition (Table 4), considering that calculations are developed under the incorrect assumption that excess functions are analytical close to the critical point, while the thermodynamic properties are, really, expressed in terms of scaling laws with universal critical exponents and universal

Table 10
Heat capacity at constant pressure, C_P^E, of pyridine(1) + n-alkane(2) mixtures

n-alkane	C_P^E ($x_1 = 0.5$; $T = 298.15$ K)			Ref.
	Exp.[a]	DQ.[b]	UNIF.[c]	
Heptane	1.27	1.25	−5.7	[78]
Decane	1.09	1.36	−8.7	[78]
Tetradecane	−0.047	0.81	−12.3	[78]
Hexadecane	−1.04	0.11	−14.	[78]

[a] Experimental result.
[b] DISQUAC values calculated with interaction parameters from Table 3.
[c] UNIFAC values calculated with interaction parameters from the literature [22,39].

Table 11
Concentration-concentration structure factor, $S_{CC}(0)$, at equimolar composition and temperature T, for pyridine(1) or methylpyridine(1) + organic solvent(2) mixtures

System[a]	T (K)	$S_{CC}(0)$		Ref.
		Exp.[b]	DQ.[c]	
PY + C_6H_6	298.15	0.278	0.278	[101]
	323.15	0.277	0.277	[101]
PY + n-C_7	298.15	1.193	1.22	[104]
	353.15	0.658	0.642	[106]
PY + methanol	298.15	0.224	0.235	[90]
	318.15	0.233	0.242	[90]
2MPY + n-C_7	313.15	0.581	0.576	[105]
3MPY + n-C_7	313.15		0.779	
2MPY + methanol	298.15	0.200	0.220	[112]
3MPY + methanol	298.15	0.217	0.226	[114]
4MPY + methanol	298.15	0.210	0.226	[114]

[a] For symbols, see Table 1.
[b] Experimental result.
[c] DISQUAC values calculated with interaction parameters from Table 3.

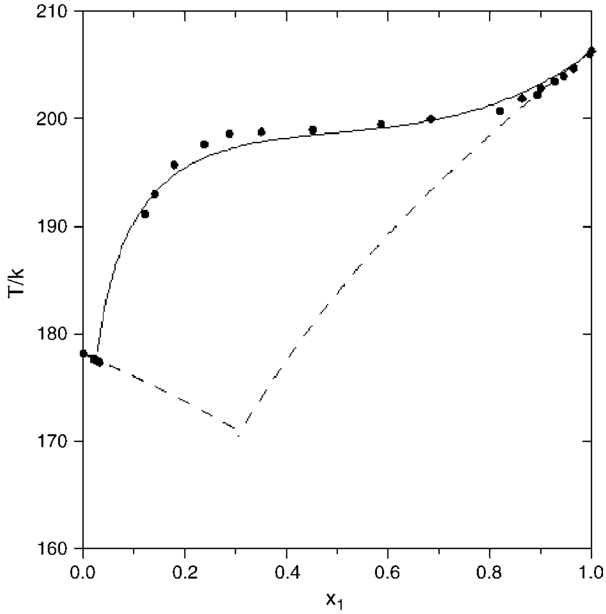

Fig. 1. SLE for the 2-methylpyridine(1) + *n*-hexane(2) mixture. Points, experimental results [115]. Solid lines, DISQUAC calculations. Dashed lines, ideal solubility curve.

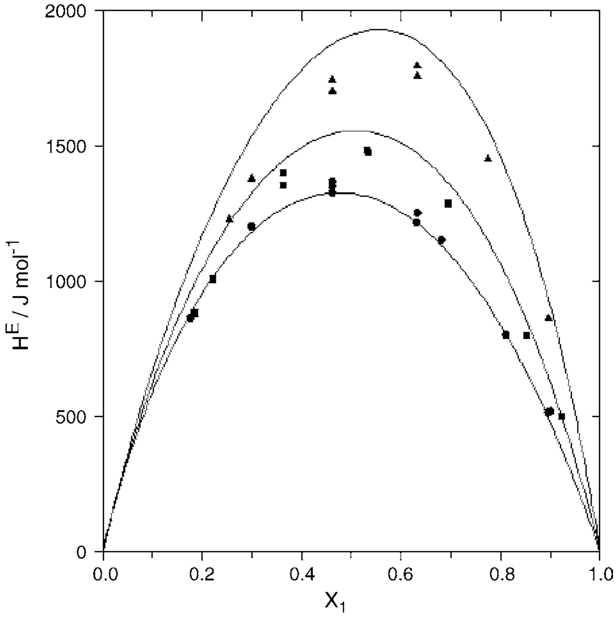

Fig. 3. H^E at 298.15 K for 2-methylpyridine(1) + alkane(2) mixtures. Points, experimental results [94]: (●), *n*-hexane; (■), *n*-decane; (▲), *n*-hexadecane; Solid lines, DISQUAC calculations.

critical functions [42]. The same occurs for other systems previously investigated: dimethyl carbonate [69], acetic anhydride [70], methanol [71], phenol [72], sulfolane [43] or alkoxyethanol [54] +alkane. The ability of DISQUAC to represent W shaped C_P^Ecurves (Fig. 7c) must be remarked and considered as a success of the model due to the theoretical importance of such curves (see below). Finally, it is noteworthy that DISQUAC can be applied to any class of system, independently of its deviation from the Raoult's law (pyridine + alkane, or +methanol). This is consistent with our previous studies on mixtures with positive [32,33,37,47,54,55,69–72] or negative [23,24,73–75] deviations from the Raoult's law. For the pyridine + benzene system, DISQUAC calculations show that this mixtures can be treated neglecting specific interactions between unlike molecules.

DISQUAC improves the theoretical results from UNIFAC (Tables 5 and 8–10). In the present case, the main shortcoming of UNIFAC is the rather poor representation of the temperature dependence of the thermodynamic properties. Systems with methylpyridines are also poorly described.

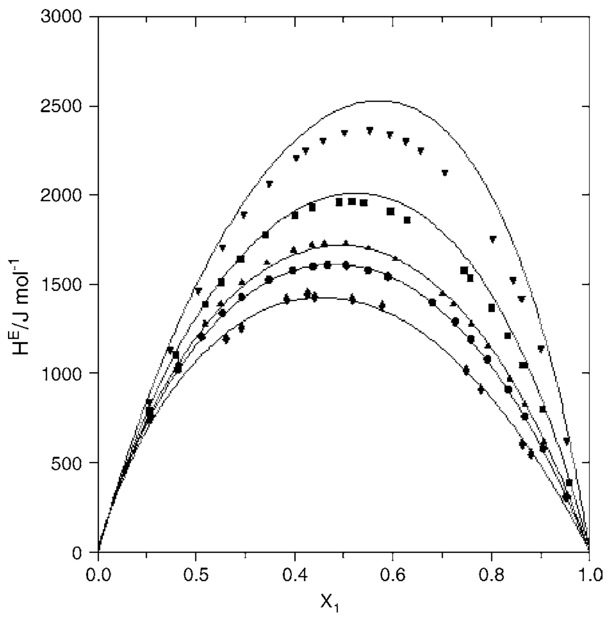

Fig. 2. H^E at 298.15 K for pyridine(1) + alkane(2) mixtures. Points, experimental results: (●), *n*-hexane; (▲), *n*-heptane; (■), *n*-decane; (▼), *n*-hexadecane [80]; (♦), cyclohexane [119]. Solid lines, DISQUAC calculations.

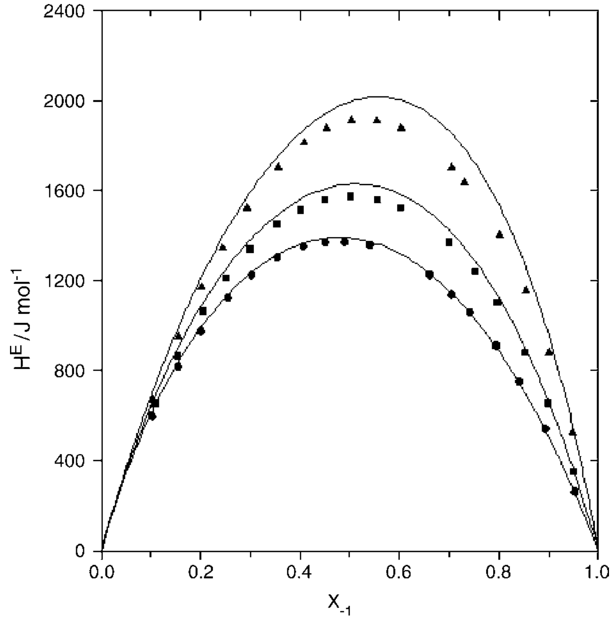

Fig. 4. H^E at 298.15 K for 3-methylpyridine(1) + alkane(2) mixtures. Points, experimental results [134]: (●), *n*-heptane; (■), *n*-decane; (▲), *n*-hexadecane; Solid lines, DISQUAC calculations.

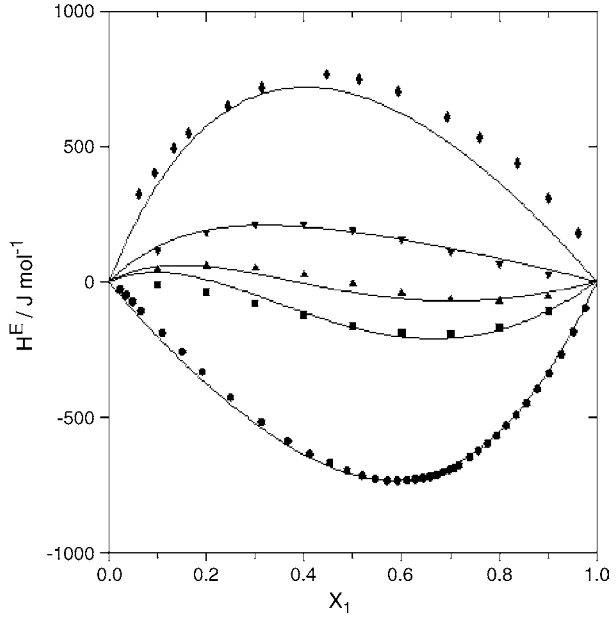

Fig. 5. H^E at 298.15 K for 1-alkanol(1) + pyridine(2) mixtures. Points, experimental results: (●), methanol [93]; (■), ethanol; (▲), 1-propanol; (▼), 1-butanol [110]; (♦), 1-octanol (T = 303.15 K) [129]. Solid lines, DISQUAC calculations.

5. Discussion

Hereafter, we are referring to values of the excess properties at equimolar composition and 298.15 K. H^E (Table 8) and V^E [76–77] of the pyridine or methylpyridine + n-alkane mixtures increase with the chain length of the alkane (Table 8). Therefore, the main contribution to these excess functions comes from the disruption of the amine-amine interactions. The large $S_{CC}(0)$ values (Table 11) show the strong homocoordination characteristic of these systems. Structural effects are present in mixtures with the shorter n-alkanes, as the S-shaped V^Ecurves reveal [76,77]. DISQUAC represents quite accurately the experimental H^E data using $C_{an,2}^{DIS/QUAC}$coefficients independent of the alkane (Table 3), which suggests that the Patterson's effect [51,52] is not present in the investigated solutions. This is supported by the fact that UNIFAC also describes these data (Table 8). In contrast, we note that for pyridine systems, the $C_{an,l}^{DIS}$ (l = 1, 3) coefficients depend on the size of the alkane (Table 3). This is necessary to describe LLE (see above) and the C_P^E curves (Fig. 7). For some mixtures, the latter show two minima and one maximum. (W shape) [78] (Fig. 7c), a typical behaviour of systems with rather large values of H^E and G^E, and compatible with mixtures not far from phase separation, i.e., mixtures where one could expect to find some degree of non-randomness [40,79]. It has been pointed out that when the maximum of $S_{CC}(0)$ is higher than 0.7 the W-shaped C_P^Emust occur [40]. However, this is not the case for the pyridine + n-heptane system.

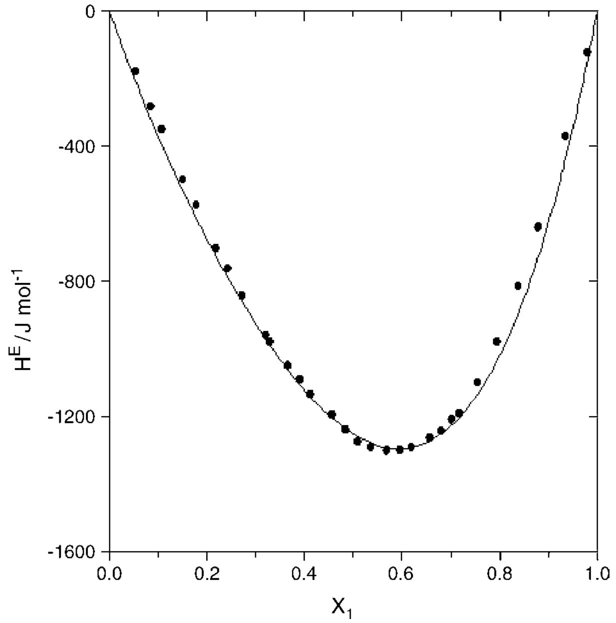

Fig. 6. H^E at 298.15 K for the methanol(1) + 2-methylpyridine(2) mixture. Points, experimental results [93]. Solid lines, DISQUAC calculations.

For mixtures including n-heptane, H^E(pyridine) = 1735 [80] >H^E(hexyalmine) = 1064 [81] >H^E(dipropylamine) = 454 [82] >H^E(triethylamine) = 112 [83] (all values in J mol^{-1}). Aniline is not miscible with alkanes at the conditions given above [84]. This means that amine-amine interactions decrease in the sequence: aniline > pyridine > hexylamine > dipropylamine > triethylamine. Note the higher values of the Trouton's constants for aniline and pyridine (Table 1). On the other hand, the miscibility gaps of aniline or pyridine + alkane systems reveal that dipolar interactions must be also present in such mixtures. The same occurs in systems formed by 1-methyl pyrrolidin-2-one [32], dimethylformamide [47], sulfolane [43], alkoxyethanol [54], or dimethylsulfoxide [85] and alkane. Dipolar interactions may roughly be evaluated in terms of $\Delta\Delta_{vap}H$, [74,85–87], the difference between $\Delta_{vap}H$ (data taken from [88,89]), of a given component with a characteristic group X and that of the homomorphic alkane. So, $\Delta\Delta_{vap}H$(aniline) = 18.2 > $\Delta\Delta_{vap}H$(cyclohexylamine) = 10.48 > $\Delta\Delta_{vap}H$(hexylamine) = 8.52 > $\Delta\Delta_{vap}H$(pyridine) = 6.48 > $\Delta\Delta_{vap}H$(dipropylamine) = 3.46 > $\Delta\Delta_{vap}H$(triethylamine) = −1.64 (all values in kJ mol^{-1}). This variation differs from that of H^E for the corresponding mixtures with heptane (see above), and suggests that the high polarizability of the aromatic ring of aniline or pyridine enhances the amine–amine interactions. This polarizability is higher in the case of aniline. Note that although $\bar{\mu}_{eff}$ (aniline) < $\bar{\mu}_{eff}$ (pyridine), $\Delta_{vap}H$ is larger for the primary amine.

For a given solvent (alkane or 1-alkanol), H^E(pyridine) > H^E(methyl pyridine) (Table 8). A similar trend is found for V^E [76,77,90,91]. So, in systems with methanol, V^E(pyridine) = −0.483 [90] >V^E(4-methylpyridine) = −0.657 [91] >V^E(2-methylpyridine) = −0.958 [90] (values given in cm^3 mol^{-1}). These V^E curves are skewed towards high mole fraction of methanol, the smaller compound, indicating the existence of free volume effects. The mentioned variation of H^E and V^E when passing from systems with pyridine to those with methylpyridines may be ascribed to the weakening of the amine-amine interactions caused by the presence of the CH_3 group in methylpyridines (steric effect), which leads to a decreasing role

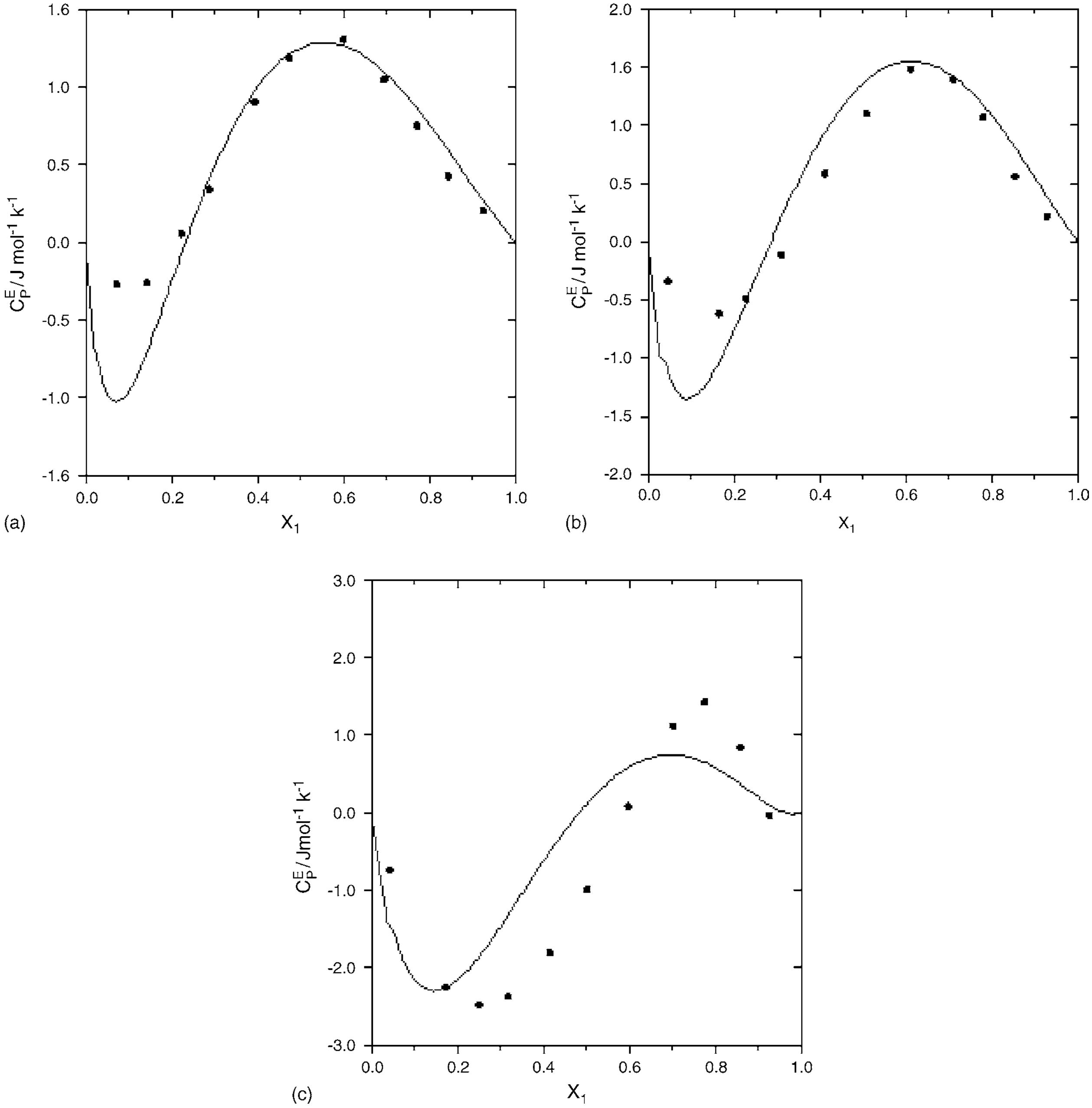

Fig. 7. C_P^E at 298.15 K for pyridine(1) + *n*-alkane(2) mixtures. Points, experimental results [78]. Solid lines, DISQUAC calculations. 7a, *n*-hexane; 7b, *n*-decane; 7c, *n*-hexadecane.

of association in the amine [92]. On the basis of the available H^E data for mixtures with alkanes, this steric effect seems to decrease in the sequence: 2MPY > 3MPY ≈ 4MPY. DISQUAC calculations on $S_{CC}(0)$ also suggest that homocoordination is weaker in systems with 2MPY. The smaller μ_{eff} value of 2MPY is here noticeable (Table 1). The lower H^E values for 1-alkanol + methylpyridine mixtures can be interpreted as a consequence of a less positive contribution to H^E from the disruption of the amine interactions. Note that the H^E difference for the systems methanol + pyridine ($H^E = -711$ J mol^{-1}) or +2-methylpyridine ($H^E = -1261$ J mol^{-1}) [93] is similar to that for the systems *n*-heptane + pyridine($H^E = 1735$ J mol^{-1} [80]), or +2MPY($H^E = 1346$ J mol^{-1} [94]). Our results on $S_{CC}(0)$ for the methanol + methylpyridine systems (Table 11) show that, for a given alcohol, this magnitude is practically independent of the methylpyridine. This may be due to the increase of homocoordination when passing from 2MPY to 3MPY or 4MPY (stronger amine-amine interactions) is compensated by an increase of heterocoordination (stronger amine-alcohol interactions). This matter is currently under investigation. Nevertheless, the higher H^E values for systems with pyridine in comparison to those for mixtures with methylpyridines has been explained [59,90] in terms of an increase of basicity of the pyridine when methyl groups are introduced [95].

Table 12
Dispersive (DIS) and quasichemical (QUAC) interchange coefficients ($l = 1$, Gibbs energy; $l = 2$, enthalpy, $l = 3$, heat capacity) for (s, n)[a] contacts in mixtures containing 1-H-imidazole

Solvent	Contact (s,n)	$C_{\mathrm{sn},1}^{\mathrm{DIS}}$	$C_{\mathrm{sn},2}^{\mathrm{DIS}}$	$C_{\mathrm{sn},1}^{\mathrm{QUAC}}$	$C_{\mathrm{sn},2}^{\mathrm{QUAC}}$	Δ[b] (K)
Benzene	(b, n)	6.5	0.65	0	0	
n-Alkane	(a, n)	6.5	1	7	14.1	
ethanol	(h, n)	−7.5	−29	−1	0.15	1.2
1-Propanol	(h, n)	−11	−29	−1	0.15	0.72
1-Butanol	(h, n)	−13	−29	−1	0.15	0.48
1-Hexanol	(h, n)	−19	−29	−1	0.15	0.70

[a] $s = \mathrm{a}$, CH_3 or CH_2 in *n*-alkanes, 1-alkanols; $s = \mathrm{b}$, C_6H_6; $s = \mathrm{h}$, OH in 1-alkanols; $s = \mathrm{n}$, N and NH in 1-H-imidazole.

[b] Result for SLE data taken from [136] and defined as in Table 7.

5.1. The interaction parameters

We note that the QUAC parameters are independent of the mixture components along each homologous series studied (e.g., pyridine + *n*-alkane, +1-alkanol, or methylpyridine + 1-alkanol, Table 3). This dependence with the molecular structure of the interaction parameters is similar to those obtained for other many mixtures previously investigated (see [32] and references herein). The different values of the $C_{\mathrm{hn},l}^{\mathrm{QUAC}}$ ($l = 1, 2$) coefficients for systems involving methanol merely reveals the different character (stronger self-association, higher dielectric constant) of first members of homologous series (methanol, ethanol, 2-methoxyethanol) [32].

The model can be applied to systems with complex molecules using information previously obtained for more simple mixtures. For example, interaction parameters for systems with crown ethers were obtained taking into account previous studies on mixtures with smaller molecules (oxane, 1,4-dioxane) [55]. Here, we present shortly the case of solutions with 1-H-imidazole, an aromatic molecule containing two amine groups (NH and N), assumed to be of the same type in the DISQUAC calculations. Due to the lack of experimental data, we have modified the interaction parameters of pyridine (Table 12) to report UCST (imidazole + heptane) = 557 K a reasonable value taking into account the high dipole moment in vapor phase of imidazole ($\mu = 6.2$ D [96]), which points out to large miscibility gaps for its mixtures with alkanes. Using these parameters and fitting only the $C_{\mathrm{hn},1}^{\mathrm{DIS/QUAC}}$ coefficients, DISQUAC correctly represents the SLE measurements of 1-H-imidazole + 1-alkanol mixtures (Table 12). Of course, the parameters obtained in such way should be taken with caution, as they can be re-calculated when more experimental data become available.

6. Conclusions

Mixtures containing pyridine or methylpyridines and organic solvents (benzene, toluene, alkane, 1-alkanol) have been investigated in the framework of DISQUAC. The model represents accurately a whole set of thermodynamic properties: VLE, LLE, SLE, G^E, H^E and C_P^E and can be applied to systems with positive or negative deviations from the Raoult's law. The replacement of pyridine by a methylpyridine leads to a weakening of the amine-amine interactions. This is attributed to the steric effect caused by the methyl group attached to the aromatic ring. The steric effect decreases in the sequence: 2MPY > 3MPY ≈ 4MPY.

Acknowledgements

Tha authors gratefully acknowledge the financial support received from the Consejería de Educación y Cultura of Junta de Castilla y León, under Project VA080/04. I. M. acknowledges the grant received from the Universidad de Valladolid.

References

[1] H. Wolff, G. Gamer, J. Phys. Chem. 76 (1972) 871–876.
[2] H. Landeck, H. Wolff, R. Götz, J. Phys. Chem. 81 (1977) 718–722.
[3] I. Cibulka, K. Tamura, I. Nagata, Fluid Phase Equilib. 39 (1988) 39–51.
[4] H. Funke, M. Wetzel, A. Heintz, Pure Appl. Chem. 61 (1989) 1429–1439.
[5] H. Wolff, H. Landeck, H.-P. Frerichs, E. Wolff, Fluid Phase Equilib. 109 (1995) 245–263.
[6] H.V. Kehiaian, K. Sosnkowska-Kehiaian, Trans. Faraday Soc. 62 (1966) 838–847.
[7] M.A. Muñoz, M. Galán, L. Gómez, C. Carmona, P. Guardado, M. Balón, Chem. Phys. 290 (2003) 69–77.
[8] E. Megiel, T. Kasprzycka-Guttman, A. Jagielska, L. Wroblewska, J. Mol. Struct. 569 (2001) 111–119.
[9] S.V. Vinogradov, R.H. Linnell, Hydrogen Bonding, Van Nostrand, Reinhold, New York, 1971.
[10] K. Sosnkowska-Kehiaian, R. Hryniewicz, H.V. Kehiaian, Bull. Acad. Pol. Sci. Ser. Sci. Chim. 17 (1969) 185–189.
[11] L. Sacconi, P. Paoletti, M. Ciampolini, J. Am. Chem. Soc. 82 (1960) 3828–3831.
[12] K.W. Morcom, D.N. Travers, Trans. Faraday Soc. 62 (1966) 2063–2068.
[13] C.W.N. Cumper, A.I. Vogel, S. Walker, J. Chem. Soc. (1956) 3621.
[14] R.K. Nigam, P.P. Singh, S. Aggarwal, S.P. Sharma, Fluid phase Equilib. 16 (1984) 25–39.
[15] H. Bertagnolli, T. Engelhardt, P. Chieux, Ber. Bunsenges. Phys. Chem. 90 (1986) 512–520.
[16] K. Sagarik, E. Spohr, Chem. Phys. 199 (1995) 73–82.
[17] T. Kasprzycka-Guttman, H. Wilczura, Thermochim. Acta 158 (1990) 1–9.
[18] E. Bich, U. Hensen, M. Michalik, D. Wandschneider, A. Heintz, Phys. Chem. Chem. Phys. 4 (2002) 5827–5832.
[19] L. Almàsy, G. Jancsó, J. Mol. Liq. 113 (2004) 61–66;
Y. Marcus, Monatsh. Chem. 132 (2001) 1387–1411.
[20] B. Wisniewska-Goclowska, S.K. Malanowski, Fluid Phase Equilib. 180 (2001) 103–113.
[21] U. Weidlich, J. Gmehling, Ind. Eng. Chem. Res. 26 (1987) 1372–1381.
[22] J. Gmehling, J. Lohmann, A. Jakob, J. Li, R. Joh, Ind. Eng. Chem. Res. 37 (1998) 4876–4882.
[23] J.A. González, I. García de la Fuente, J.C. Cobos, Fluid Phase Equilib. 168 (2000) 31–58.
[24] J.A. González, I. García de la Fuente, J.C. Cobos, Can. J. Chem. 78 (2000) 1272–1284.
[25] N. Riesco, S. Villa, J.A. González, I. García de la Fuente, J.C. Cobos, Fluid Phase Equilib. 202 (2002) 345–358.
[26] S. Villa, J.A. González, I. García de la Fuente, N. Riesco, J.C. Cobos, J. Solution Chem. 31 (2002) 1019–1038.
[27] N. Riesco, J.A. González, S. Villa, I. García de la Fuente, J.C. Cobos, Phys. Chem. Liq. 41 (2003) 309–321.
[28] J.A. González, I. Mozo, I. García de la Fuente, J. C. Cobos, Can J. Chem., in press.
[29] H.V. Kehiaian, Fluid Phase Equilib. 13 (1983) 243–252;
H.V. Kehiaian, Pure Appl. Chem. 57 (1985) 15–30.

[30] E.A. Guggenheim, Mixtures Oxford University Press, London, 1952.
[31] J.C. Cobos, Fluid Phase Equilib. 133 (1997) 105–127.
[32] J.A. González, U. Domanska, J. Lachwa, Can. J. Chem. 81 (2003) 1451–1461.
[33] J.A. González, J.C. Cobos, I. García de la Fuente, J. Mol. Liq. 115 (2004) 93–103.
[34] A. Bondi, Physical Properties of Molecular Crystals, Liquids and Glasses, Wiley, New York, 1968.
[35] H.V. Kehiaian, J.-P.E. Grolier, G.C. Benson, J. Chim. Phys. 75 (1978) 1031–1048.
[36] J.A. González, I. García de la Fuente, J.C. Cobos, C. Casanova, A. Ait-Kaci, Fluid Phase Equilib. 112 (1995) 63–87.
[37] J.A. González, I. García, J.C. Cobos, C. Casanova, Ber. Bunsenges. Phys. Chem. 95 (1991) 1658–1668.
[38] A. Fredenslund, R.L. Jones, J.M. Prausnitz, AIChE J. 21 (1975) 1086–1099.
[39] J. Gmehling, J. Li, M. Schiller, Ind. Eng. Chem. Res. 32 (1993) 178–193.
[40] R.G. Rubio, M. Cáceres, R.M. Masegosa, L. Andreoli-Ball, M. Costas, D. Patterson, Ber. Bunsenges. Phys. Chem. 93 (1989) 48–56.
[41] A.B. Bhatia, D.E. Thorton, Phys. Rev. B. 2 (1970) 3004–3012.
[42] J.S. Rowlinson, F.L. Swinton, Liquids and Liquid Mixtures, third ed., Butterworths, London, 1982.
[43] J.A. González, U. Domanska, Phys. Chem. Chem. Phys. 3 (2001) 1034–1042.
[44] P.R. Garrett, J.M. Pollock, J. Chem. Thermodyn. 9 (1977) 561–566.
[45] O. Dahmani, A. Ait-Kaci, J. Jose, J. Thermal Anal. 41 (1994) 833–847.
[46] P.R. Garrett, J.M. Pollock, K.W. Morcom, J. Chem. Thermodyn. 5 (1973) 569–575.
[47] J.A. González, J.C. Cobos, I. García de la Fuente, Fluid Phase Equilib. 224 (2004) 169–183.
[48] P.R. Garrett, J.M. Pollock, K.W. Morcom, J. Chem. Thermodyn. 3 (1971) 135–141.
[49] J.N. Murrell, V.M.S. Gil, Trans. Faraday Soc. 61 (1965) 402–407.
[50] A. Ait-Kaci, Ph.D. thesis, Lyon (France) (1982).
[51] M. Costas, D. Patterson, Thermochim. Acta 120 (1987) 161–181.
[52] D. Patterson, J. Solution Chem. 23 (1994) 105–120.
[53] O. Dahmani, A. Ait-Kaci, J. Thermal Anal. 44 (1995) 385–393.
[54] J.A. González, J.C. Cobos, F.J. Carmona, I. García de la Fuente, V.R. Bhethanabotla, S.W. Campbell, Phys. Chem. Chem. Phys. 3 (2001) 2856–2865.
[55] U. Domanska, J.A. González, Fluid Phase Equilib. 205 (2003) 317–338.
[56] J.A. González, I. García de la Fuente, J.C. Cobos, C. Casanova, Fluid Phase Equilib. 93 (1994) 1–22.
[57] U. Domanska, J.A. González, Fluid Phase Equilib. 119 (1996) 131–151.
[58] J.A. González, I. García de la Fuente, J.C. Cobos, Can. J. Chem. 76 (1998) 1418–1428.
[59] J. Abe, K. Nakanishi, H. Touhara, J. Chem. Thermodyn. 10 (1978) 483–494.
[60] T. Kasprzycka-Guttman, M. Jarosz-Jarszewska, A. Myslinski, J. Thermal Anal. 45 (1995) 751–759.
[61] J.A. González, J. Carmona, I. García de la Fuente, J.C. Cobos, Thermochim. Acta 326 (1999) 53–67.
[62] U. Domanska, J.A. González, Fluid Phase Equilib. 123 (1996) 167–187.
[63] A. Orszagh, T. Kasprzycka-Guttman, Bull. Acad. Pol. Sci. Ser. Sci. Chim. 20 (1972) 349–354.
[64] A. Orszagh, T. Kasprzycka-Guttman, Bull. Acad. Pol. Sci. Ser. Sci. Chim. 20 (1972) 354–360.
[65] A. Orszagh, T. Kasprzycka-Guttman, Bull. Acad. Pol. Sci. Ser. Sci. Chim. 22 (1974) 625–629.
[66] A. Orszagh, T. Kasprzycka-Guttman, Bull. Acad. Pol. Sci. Ser. Sci. Chim. 22. (1974).
[67] B. Semeniuk, T. Kasprzycka-Guttman, J. Chem. Thermodyn. 20 (1988) 1427–1431.
[68] T. Kasprzycka-Guttman, I. Chojnacka, J. Chem. Thermodyn. 21 (1989) 721–725.
[69] J.A. González, I. García de la Fuente, J.C. Cobos, C. Casanova, H.V. Kehiaian, Thermochim. Acta 217 (1993) 57–69.
[70] M. Aboy, S. Villa, N. Riesco, J.A. González, I. García de la Fuente, J.C. Cobos, J. Chem. Eng. Data 47 (2002) 950–953;
H.V. Kehiaian, J.A. González, I. García, R. Escarda, J.C. Cobos, C. Casanova, Fluid Phase Equilib. 69 (1991) 91–98.
[71] J.A. González, I. García de la Fuente, J.C. Cobos, Ber. Bunsenges. Phys. Chem. 101 (1997) 219–227.
[72] J.A. González, I. García de la Fuente, J.C. Cobos, Ber. Bunsenges. Phys. Chem. 100 (1996) 1746–1751.
[73] J.A. González, I. García de la Fuente, J.C. Cobos, J. Chem. Soc. Faraday Trans. 93 (1997) 3773–3780.
[74] J.A. González, I. García de la Fuente, J.C. Cobos, Phys. Chem. Chem. Phys. 1 (1999) 275–283.
[75] J.A. González, I. Mozo, I. García de la Fuente, J.C. Cobos, Phys. Chem. Liq. 43 (2005) 317–332.
[76] T. Kasprzycka-Guttman, H. Kurcinska, J. Solution Chem. 18 (1989) 727–734.
[77] T. Kasprzycka-Guttman, H. Kurcinska, Thermochim. Acta 173 (1990) 63–70.
[78] A. Laínez, M.M. Rodrigo, E. Wilhelm, J.-P.E. Grolier, J. Solution Chem. 21 (1992) 49–65.
[79] L.M. Trejo, M. Costas, D. Patterson, J. Chem. Soc. Faraday Trans. 87 (1991) 3001–3008.
[80] R. Kechavarz, J.-P. Dubes, H. Tachoire, Int. DATA Ser. Sel. Data Mixtures Ser. A. 20 (1992) 11–17.
[81] R. Pfestorf, D. Kuchenbecker, K. Quitzsch, Z. Phys. Chem. (Leipzig) 263 (1982) 233–240.
[82] M.I. Paz Andrade, F. Sarmiento, Int. Data Ser. Selected Data Mixtures, Ser. A. (1984) 110.
[83] M. Bender, J. Hauser, A. Heintz, Ber. Bunsenges. Phys. Chem. 95 (1991) 801–811.
[84] H. Matsuda, K. Ochi, K. Kojima, J. Chem. Eng. Data 48 (2003) 184–189.
[85] J.A. González, S. Villa, N. Riesco, I. García de la Fuente, J.C. Cobos, Phys. Chem. Liq. 41 (2003) 583–597.
[86] H.V. Kehiaian, M.R. Tiné, L. Lepori, E. Matteoli, B. Marongiu, Fluid Phase Equilib. 46 (1989) 131–177.
[87] J.A. González, I. García de la Fuente, J.C. Cobos, Fluid Phase Equilib. 154 (1999) 11–31.
[88] V. Majer, V. Svoboda, Enthalpies of Vaporization of Organic Compounds, Blackwell, Oxford, 1985.
[89] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents, in: A. Weissberger (Ed.), Techniques of Chemistry, 2, Wiley, New York, 1986.
[90] K. Nakanishi, K. Ashitani, H. Touhara, J. Chem. Thermodyn. 8 (1976) 121–126.
[91] P. Haraschta, A. Heintz, J.K. Lehmann, A. Peters, J. Chem. Eng. Data 44 (1999) 932–935.
[92] A.J. Treszczanowicz, D. Patterson, G.C. Benson, T. Kasprzycka-Guttman, Fluid Phase Equilib. 50 (1989) 235–247.
[93] H. Touhara, K. Nakanishi, J. Chem. Thermodyn. 17 (1985) 909–914.
[94] J.C. Merlin, A. Ait-Kaci, Int. DATA Ser. Sel. Data Mixtures Ser. A. 9 (1981) 140–145.
[95] H.C. Brown, X.R. Mihm, J. Am. Chem. Soc. 77 (1955) 1723–1726.
[96] A.L. McClellan, Tables of Experimental Dipole Moments, Rahara Enterprises, El Cerrito, CA, 1974.
[97] E. Wilhelm, Thermochim. Acta 162 (1990) 43–57.
[98] A. Heintz, P.K. Naicker, S.P. Verevkin, R. Pfestorf, Ber. Bunsenges. Phys. Chem. 102 (1998) 953–959.
[99] R.C. Reid, J.M. Prausnitz, B.E. Poling, The Properties of Gases and Liquids, fourth ed., McGraw Hill, N.Y, 1987.
[100] M.R. Tiné, H.V. Kehiaian, Fluid Phase Equilib. 32 (1987) 211–248.
[101] J. Jose, C. Michou-Saucet, M.A. Michou-Saucet, Int. DATA Ser. Sel. Data Mixtures Ser. A. 16 (1988) 37–42.
[102] A. Ait-Kaci, H.V. Kehiaian, Int. DATA Ser. Sel. Data Mixtures Ser. A. 13 (1985) 41–51.

[103] M. Rogalski, A. Bylicki, J. Chem. Thermodyn. 17 (1985) 915–919.

[104] M.A. Michou-Saucet, J. Jose, C. Michou-Saucet, Int. DATA Ser. Sel. Data Mixtures Ser. A. 14 (1986) 140–145.

[105] S. Warycha, J. Chem. Eng. Data 38 (1993) 274–276.

[106] Z. Maczynska, Int. DATA Ser. Sel. Data Mixtures Ser. A. 8 (1980) 104–115.

[107] P.P. Singh, P.P. Sharma, B.R. Sidhu, Aust. J. Chem. 30 (1977) 1241–1247.

[108] S. Warycha, Z. Phys. Chem. (Leipzig) 258 (1977) 873–878.

[109] J.L. Oscarson, S.O. Lundell, J.R. Cunningham, AIChE Syposium Ser., 83 (1987) 1-17.

[110] T.J.V. Findlay, J.L. Copp, Trans. Faraday Soc. 65 (1969) 1463–1469.

[111] M. Rogalski, J. Chem. Thermodyn. 17 (1985) 1045–1049.

[112] K. Nakanishi, Int. DATA Ser. Sel. Data Mixtures Ser. A. 28 (2000) 248–269.

[113] M. Rogalski, J. Chem. Thermodyn. 17 (1985) 921–926.

[114] S. Warycha, Z. Phys. Chem. (Leipzig) 258 (1977) 864–872.

[115] A. Ait-Kaci, J.-C. Merlin, Int. DATA Ser. Sel. Data Mixtures Ser. A. 7 (1979) 67–70.

[116] W. Woycicki, K.W. Sadowska, Bull. Acad. Pol. Sci. Ser. Sci. Chim. 16 (1968) 329–334.

[117] T. Kasprzycka-Guttman, H. Wilczura, Thermochim. Acta 225 (1993) 31–36.

[118] W. Woycicki, J. Chem. Thermodyn. 6 (1974) 141–147.

[119] D. Díez, B. Ruiz, F.M. Royo, C. Gutiérrez Losa, J. Chem. Thermodyn. 17 (1985) 371–377.

[120] T. Murakami, S. Murakami, R. Fujishiro, Bull. Chem. Soc. Jpn. 42 (1969) 35–40.

[121] T.J.V. Findlay, Aust. J. Chem. 14 (1961) 646–648.

[122] P.P. Singh, D.V. Verma, Thermochim. Acta 13 (1975) 89–92.

[123] H. Wilczura, T. Kasprzycka-Guttman, J. Thermal Anal. 35 (1989) 2441–2446.

[124] W. Woycicki, K.W. Sadowska, Bull. Acad. Pol. Sci. Ser. Sci. Chim. 16 (1968) 147–153.

[125] P.P. Singh, S.P. Sharma, Thermochim. Acta 88 (1985) 467–484.

[126] D. Barès, M. Souliè, J. Metzger, J. Chim. Phys. Phys. Chim. Biol. 70 (1973) 1531–1539.

[127] P.P. Singh, D.V. Verma, P.S. Arora, Thermochim. Acta 15 (1976) 267–280.

[128] T. Kasprzycka-Guttman, A. Myslinski, H. Wilczura, J. Thermal Anal. 29 (1984) 173–177.

[129] T. Kasprzycka-Guttman, K. Izycka, J. Chem. Thermodyn. 9 (1977) 403–405.

[130] J.-C. Merlin, A. Ait-Kaci, Int. DATA Ser. Sel. Data Mixtures Ser. A. 10 (1982) 28–34.

[131] T. Kasprzycka-Guttman, H. Wilczura, A. Myslinski, J. Thermal Anal. 38 (1992) 1357–1364.

[132] T. Kasprzycka-Guttman, K. Izycka, M. Kurzela, J. Thermal. Anal. 14 (1978) 127–130.

[133] T. Kasprzycka-Guttman, H. Wilczura, Thermochim. Acta 198 (1992) 405–412.

[134] R. Kechavarz, J.-P. Dubes, H. Tachoire, Int. DATA Ser. Sel. Data Mixtures Ser. A. 20 (1992) 18–31.

[135] T. Kasprzycka-Guttman, H. Wilczura, Thermochim. Acta 184 (1991) 321–327.

[136] U. Domanska, M. Kozlowska, M. Rogalski, J. Chem. Eng. Data 47 (2002) 8–10.