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Thermodynamics of mixtures containing amines
VII. Systems containing dimethyl or trimethylpyridines

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Abstract

Mixtures with dimethyl or trimethylpyridines and alkane, aromatic compound or 1-alkanol have been examined using different theories: DISQUAC, Flory, the concentration–concentration structure factor, $S_{CC}(0)$, or the Kirkwood–Buff formalism. DISQUAC represents fairly well the available experimental data, and improves theoretical calculations from Dortmund UNIFAC. Two important effects have been investigated: (i) the effect of increasing the number of methyl groups attached to the aromatic ring of the amine; (ii) the effect of modifying the position of the methyl groups in this ring. The molar excess enthalpy, H^E, and the molar excess volume, V^E, decrease in systems with alkane or methanol as follows: pyridine > 3-methylpyridine > 3,5-dimethylpyridine and pyridine > 2-methylpyridine > 2,4-dimethylpyridine > 2,4,6-trimethylpyridine, which has been attributed to a weakening of the amine–amine interactions in the same sequences. This is in agreement with the relative variation of the effective dipole moment, $\bar{\mu}$, and of the differences between the boiling temperature of a pyridine base and that of the homomorphic alkane. For heptane solutions, the observed H^E variation, H^E (3,5-dimethylpyridine) > H^E (2,4-dimethylpyridine) > H^E (2,6-dimethylpyridine), is explained similarly. Calculations on the basis of the Flory model confirm that orientational effects become weaker in systems with alkane in the order: pyridine > methylpyridine > dimethylpyridine > trimethylpyridine. $S_{CC}(0)$ calculations show that steric effects increase with the number of CH_3– groups in the pyridine base, and that the steric effects exerted by methyl groups in positions 2 and 6 are higher than when they are placed in positions 3 and 5. The hydrogen bond energy in methanol mixtures is independent of the pyridine base, and it is estimated to be $-35.2\ \mathrm{kJ\ mol^{-1}}$. Heterocoordination in these solutions is due in part to size effects. Their structure is nearly random. The values of the local mole fractions calculated from the Kirkwood–Buff theory support this conclusion as they are close to the bulk ones.

Keywords: Thermodynamics; Pyridine base; Models; Interactions; Structural effects; Steric hindrance

1. Introduction

In order to gain insight into the liquid state, thermodynamic properties such as H^E, V^E, or isobaric excess molar heat capacity, C_P^E, of liquid mixtures can be examined taking into account differences in molecular size and shape, anisotropy, dispersion, polarity, polarizability, association, which may be included in terms of hydrogen bonds or charge transfer, and so forth. In many mixtures, dipolar (and even quadrupolar) interactions contribute significantly to the thermodynamic properties. A polar substance is defined as a compound with a permanent electric dipole moment in gas phase, μ. For the purpose of characterizing the effective polarity of a single, isolated molecule, one may define a reduced dipole moment according to [1,2]

$$\hat{\mu} = \left[\frac{\mu^2}{4\pi\varepsilon_0\sigma^3\varepsilon}\right]^{1/2} \tag{1}$$

where ε_0 is the permittivity of the vacuum, σ an appropriate molecular size parameter and ε the corresponding interaction energy parameter. Eq. (1) may advantageously be transformed by virtue of the corresponding states principle to

$$\mu^* = \left[\frac{\mu^2 P_c}{4\pi\varepsilon_0 k_B^2 T_c^2}\right]^{1/2} \tag{2}$$

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where k_B, P_c and T_c stand for the Boltzmann's constant, critical pressure and critical temperature, respectively. If we are interested on the impact of polarity on bulk properties, the appropriate quantity to be used is [1]

$$\bar{\mu} = \left[\frac{\mu^2 N_A}{4\pi\varepsilon_0 V k_B T}\right]^{1/2} \tag{3}$$

which may be called as the effective dipole moment (N_A is the Avogadro's number; V the molar volume and T is the system temperature). While for a given series (say 1-alkanols), μ varies only slightly with the chain length, by necessity μ^* or $\bar{\mu}$ show much greater variation (see, e.g. [3]) In addition, interactions between molecules in pure liquids may be investigated *via* the differences between the boiling temperature, ΔT_b (or the standard enthalpy of vaporization) of a given compound with a characteristic group Z and that of the homomorphic alkane [4,5].

Primary and secondary amines are weakly self-associated [6–12]. Pyridine and its alkyl derivatives are examples of tertiary heterocyclic amines. Their Trouton's constants are rather similar (Table 1) and show values close to that of non-associated species (92.05 J mol^{-1} K^{-1}; for 1-alkanols, this constant is 110.88 J mol^{-1} K^{-1} [13]). Nevertheless, ΔT_b and $\bar{\mu}$ values (Table 1) indicate that interactions between amine molecules are stronger in pyridine than in, e.g., 2,6-dimethylpyridine or 2,4,6-trimethylpyridine. Association of pyridine has been the subject of many studies in such way that different association mechanisms have been proposed [14–18]. 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 [15,16]. 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 [17,18]. The existence of pyridine dimers, which seems to be supported by X-ray and neutron diffraction [19] and by statistical mechanical simulation [20], 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.

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 $CH_3(CH_2)_nN(CH_2)_mCH_3$) allow the study of the size and steric effects produced by alkyl-groups 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 alkyl derivatives are 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 [12].

Many different theories may be used to characterize interactions in liquid mixtures or to predict/correlate their thermodynamic properties. DISQUAC [21], UNIFAC (Dortmund version) [22,23] and Flory [24] are physical theories where association is not considered in a specific manner. DISQUAC (*dis*persive-*qua*si*c*hemical) is a group contribution model based on the rigid lattice theory developed by Guggenheim [25], which uses interaction parameters dependent on the molecular structure. Although this means one has to leave the classical concept of group contribution model, it is essential for practical purposes. As a matter of fact, it leads to improved predictions in the case of systems involving branched or cyclic molecules, or molecules where proximity (intramolecular) effects are present. Under the mentioned basic assumption, we have shown that the model can be applied to any type of liquid mixture: 1-alkanol [26]; linear monocaboxylic acid [27], or hydroxyether [28] + alkane; 1-alkanol + amine [3]; amide + alkane or + 1-alkanol [29]. The model provides an accurate representation of thermodynamic properties (vapor–liquid (VLE), liquid–liquid (LLE) and solid–liquid (SLE) equilibria, H^E or C_P^E) of binary systems. DISQUAC also yields accurate predictions on VLE and H^E of ternary mixtures using information from the constituent binaries only, i.e., neglecting ternary interactions [30]. UNIFAC [22] (*UNI*QUAC *f*unctional-group *ac*tivity coefficients) is a classical group contribution model,

Table 1
Physical constants[a] of pure pyridines

Amine	V (cm^3 mol^{-1})	T_b (K)	$\Delta_{vap}H$ (kJ mol^{-1})	$\Delta_{vap}H/T_b$ (J mol^{-1} K^{-1})	ΔT_b (K)	μ (D)	$\bar{\mu}$
Pyridine	80.86[b]	388.4[c]	35.09[c]	90.3	35.2	2.37[b]	1.008
2-Methylpyridine	99.09[b]	402.6[c]	36.17[c]	89.8	18.8	1.97[b]	0.757
3-Methylpyridine	97.83[b]	417.3[c]	37.35[c]	89.5	33.5	2.4[b]	0.929
4-Methylpyridine	98.01[b]	418.5[c]	37.51[c]	89.6	34.7	2.6[b]	1.005
2,4-Dimethylpyridine	115.67[d]	431.5[b]	38.53[c]	89.3	19.2	2.3[b]	0.819
2,6-Dimethylpyridine	116.73[d]	417.2[b]	37.46[c]	89.8	4.9	1.66[b]	0.588
3,5-Dimethylpyridine	113.11[e]	444.6[c]	39.46[c]	88.7	32.3	2.5[f]	0.899
2,4,6-Trimethylpyridine	132.80[d]	444.2[b]	39.87[c]	89.7	6.3	2.05[b]	0.680

[a] V: molar volume at 298.15 K; T_b: boiling point; $\Delta_{vap}H$: standard enthalpy of vaporization at T_b; ΔT_b: difference between T_b of a given pyridine and that of the isomeric aromatic compound [103]; μ: dipole moment; $\bar{\mu}$: effective dipole moment (Eq. (3)).

[b] [103].

[c] [104].

[d] [80].

[e] [84].

[f] [105].

where interaction parameters are independent of the molecular structure. Its main advantage is related to the large matrix of interaction parameters available, which makes possible the application of the model to a large variety of systems. UNIFAC results are usually somewhat poorer than those obtained from DISQUAC, particularly when the temperature dependence of the thermodynamic properties must be accurately described (e.g., for LLE and C_P^E).

In the framework of the DISQUAC and UNIFAC models, it is assumed that there is no variation of volume upon mixing ($V^E = 0$). The Flory model [24], where random mixing is an essential hypothesis, is a free volume theory, which leads to an equation of state. Therefore, it is possible to obtain information simultaneously on H^E and V^E. The model provides good results for systems formed by one slightly polar component (*N,N,N*-trialkylamine [31] or monoether [32] + alkane), or involving two polar compounds as 1-alkanol + 1-alkanol [33] or 2-methoxyethanol + alkoxyethanol [34], i.e. for mixtures where random mixing is expected. Recently, we have shown that the model can be also successfully used to investigate orientational effects present in a given solution by studying the concentration dependence of the energetic parameter χ_{12} of the theory [35]. The ERAS (*e*xtended *r*eal *a*ssociation *s*olution) model [36] combines the real association solution theory [37] with a physical term, represented by the Flory equation of state. It also provides information on H^E and V^E, and has been applied successfully to mixtures with self-associated components (1-alkanol + alkane [36]), or to systems where complex formation is expected (1-alkanol + amine [3,9,38,39]).

On the other hand, it is very interesting to link the thermodynamic properties of liquid mixtures with their microscopic structural description, and particularly with local deviations from the bulk composition. The study of fluctuations in composition in multicomponent mixtures is a standard topic in statistical mechanics [40,41]. There are at least two ways of looking at the fluctuations in a binary mixture [40–42]. We either consider the fluctuations in the number of molecules N_1 and N_2 ($N_1 + N_2 = N$) of each component and the cross fluctuations $\langle \Delta N_i \Delta N_j \rangle$ ($i, j = 1, 2$) or we study the fluctuations in the number of molecules regardless of the components $\langle \Delta N^2 \rangle$, the fluctuations in the mole fraction $\langle \Delta x^2 \rangle$ and the cross fluctuations. In each case, $\langle\ \rangle$ stands for an ensemble average, in the grand canonical ensemble. The first of these approaches was followed by Kirkwood and Buff [43–45]. The second approach was developed by Bhatia and Thorton [46] and used in the study of liquid binary alloys [47,48] on the basis of the so-called Bhatia–Thorton partial structure factors. This approach was generalized [49–51] in order to provide a rationale which links the asymptotic behaviour of the ordering potential to the interchange energy parameters in the semi-phenomenological theories of thermodynamic properties of liquid mixtures [49–53]. More recently, Cobos has discussed the correlation between the concentration–concentration structure factor with C_V^E (isochoric excess molar heat capacity) and C_P^E [41].

Mixtures including pyridines have been studied in terms of different theories. So, systems with alkanes or 1-butanol have been investigated in terms of the ERAS model [54,55] and aqueous solutions using the Kirkwood–Buff theory [56,57]. Unfortunately, ERAS does not represent the symmetry of the H^E curves of mixtures involving alkanes. The UNIQUAC equation was modified to predict accurately VLE data over a wide range of temperature [58]. In the framework of UNIFAC (Dortmund version), interaction parameters for contacts between the pyridine group and other different groups are available [23]. In a recent work [59], we have studied pyridine systems in terms of DISQUAC. We have shown that the model describes rather accurately a whole set of thermodynamic properties such as VLE, G^E, LLE, SLE, or H^E over a wide range of temperature. An important result is that DISQUAC also predicts the w-shaped C_P^E of the pyridine + hexadecane mixture [60].

The purpose of this work is to gain insight into the interactions and molecular structure of systems containing dimethyl or trimethylpyridine and a solvent as alkane, aromatic compound or 1-alkanol on the basis of the theories mentioned above.

2. Theories

2.1. DISQUAC

In the framework of DISQUAC, mixtures with alkyl derivatives of pyridine and an organic solvent are regarded as possessing the following four types of surface: (i) type n, N in the amine; (ii) type b, aromatic ring in the pyridine bases studied (C_5H_3 or C_5H_2) or in benzene and in its alkyl derivatives (toluene, dimethylbenzene, trimethylbenzene); (iii) type a, aliphatic (CH_3, CH_2, in alkanes, alkyl derivatives of benzene or pyridine, or in 1-alkanols); (iv) type h, OH, in 1-alkanols.

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 [61]. As volume and surface units, the volume R_{CH4} and surface Q_{CH4} of methane are taken arbitrarily [62]. The geometrical parameters for the groups referred to in this work are given elsewhere [59]. (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 [62,63] must be considered. Thus

$$G^E = G^{E,COMB} + G^{E,DIS} + G^{E,QUAC} \quad (4)$$

$$H^E = H^{E,DIS} + H^{E,QUAC} \quad (5)$$

(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 removed via the hypothesis of considering structure dependent interaction parameters.

The equations used to calculate the DIS and QUAC contributions to $G^{\mathrm{E}}$and H^{E} in the framework of DISQUAC are given elsewhere [26]. The temperature dependence of the interaction parameters is expressed in terms of the DIS and QUAC interchange coefficients [26], $C_{\mathrm{st},l}^{\mathrm{DIS}}$; $C_{\mathrm{st},l}^{\mathrm{QUAC}}$ 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 [22] differs from the original UNIFAC [64] 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

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{COMB}} + \ln \gamma_i^{\mathrm{RES}} \tag{6}$$

where $\ln \gamma_i^{\mathrm{COMB}}$ is the combinatorial term and $\ln \gamma_i^{\mathrm{RES}}$ is the residual term. Equations are given elsewhere [3].

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 [23]. Previously, pyridine was considered as homogeneous molecule [65]. 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 [23,65].

2.3. Flory model

A rather detailed description of this model has been reported elsewhere [24,35,66], together with the equations needed to calculate H^{E} and V^{E}. It is remarkable that V^{E} can be calculated because the molar volume of the mixture is known from the equation of state, valid for pure compounds and for the mixtures. In its reduced form, this equation of state is

$$\frac{\bar{P}_i \bar{V}_i}{\bar{T}_i} = \frac{\bar{V}_i^{1/3}}{\bar{V}_i^{1/3} - 1} - \frac{1}{\bar{V}_i \bar{T}_i} \quad i = 1, 2 \text{ and M (mixture)} \tag{7}$$

where $\bar{P}_i = P/P_i^*$; $\bar{V}_i = V_i/V_i^*$ and $\bar{T}_i = T/T_i^*$ are the reduced parameters and $P_i^*, V_i^*, T_i^*$are the corresponding reduction parameters, which for pure components can be obtained from experimental data, such as the coefficients of thermal expansion, and the isothermal compressibility. In the case of mixtures, these parameters are calculated using certain mixing rules [35], where the parameter χ_{12}, typically obtained from H^{E} data, is introduced.

If the random mixing hypothesis is valid, $\chi_{12} = \chi_{12}(\text{Flory})$, and this value is independent of the concentration. On the contrary, if orientational effects are present in the mixture, χ_{12} depends on the mole fraction. We express this fact, writing explicitly $\chi_{12}(x_1)$. Now, two cases are possible: (i) $\chi_{12}(x_1) > \chi_{12}$, which is equivalent to the number of interactions between contact sites of different molecules is lower than that predicted by Flory model. (ii) $\chi_{12}(x_1) < \chi_{12}$ and the number of interactions between contact sites of different molecules is higher than the corresponding to the random mixing hypothesis. For more details, see [35].

2.4. Concentration–concentration structure factor

Mixture structure can be studied using the $S_{\mathrm{CC}}(0)$ function [41], defined as [41,42,46]

$$S_{\mathrm{CC}}(0) = \frac{RT}{(\partial^2 G^{\mathrm{M}}/\partial x_1^2)_{\mathrm{P,T}}} = \frac{x_1 x_2}{D} \tag{8}$$

with

$$D = \frac{x_1 x_2}{RT}\left(\frac{\partial^2 G^{\mathrm{M}}}{\partial x_1^2}\right)_{\mathrm{P,T}} = 1 + \frac{x_1 x_2}{RT}\left(\frac{\partial^2 G^{\mathrm{E}}}{\partial x_1^2}\right)_{\mathrm{P,T}} \tag{9}$$

D is a function closely related to thermodynamic stability [2,42]. 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.

In terms of the DISQUAC model

$$\frac{D}{x_1 x_2} = \frac{1}{S_{\mathrm{CC}}(0)} = \frac{1}{x_1 x_2} + \frac{1}{RT}\left(\frac{\partial^2 G^{\mathrm{E,COMB}}}{\partial x_1^2}\right)_{\mathrm{P,T}} + \frac{1}{RT}\left(\frac{\partial^2 G^{\mathrm{E,INT}}}{\partial x_1^2}\right)_{\mathrm{P,T}} \tag{10}$$

where $G^{\mathrm{E,INT}} = G^{\mathrm{E,DIS}} + G^{\mathrm{E,QUAC}}$. Expressions for $(\partial^2 G^{\mathrm{E,COMB}}/\partial x_1^2)_{\mathrm{P,T}}$ and $(\partial^2 G^{\mathrm{E,INT}}/\partial x_1^2)_{\mathrm{P,T}}$ have been given elsewhere [67]. The combinatorial part only depends on r_i values and mole fractions [67], it is always positive and hence causes heterocoordination.

2.5. Kirkwood–Buff integrals

The theory [44,45] describes thermodynamic properties of solutions in an exact manner in the whole concentration range using the values

$$G_{ij} = \int_0^\infty (g_{ij} - 1)4\pi r^2 \, \mathrm{d}r \tag{11}$$

which are called the Kirkwood–Buff integrals. The radial distribution function, g_{ij}, denotes the probability of finding a molecule of species i in a volume element at the distance r of the center of a molecule of species j. So, this function provides information about the solution structure on the microscopic level. The product $\rho_j G_{ij}$ (ρ_j is the number density of molecules of species j) represents the average excess (or deficiency) number of molecules j in the whole space around a molecule i with respect to the bulk average. So, G_{ij} values can be obtained from $\rho_j G_{ij}$ by a process of normalization with respect to concentration and can be interpreted as follows: $G_{ij} > 0$ represents the excess of molecules of the i type in the space around a given molecule of species j. This means attractive interactions between molecules of i and j. $G_{ij} < 0$ means that interactions of i–i and j–j are preferred to mutual interactions [44,57]. The Kirkwood–Buff integrals can be derived from experimental data of thermodynamic properties as chemical potential; partial molar volumes and isothermal compressibility factor. Due to the lack of experimental data, the isothermal compressibility of the mixtures is calculated in this work as $\kappa_T = \Phi_1\kappa_{T1} + \Phi_2\kappa_{T2}$, where $\Phi_i (= x_i V_i/(x_1 V_1 + x_2 V_2))$ is the volume fraction of the component i of the system, and κ_{Ti} is its isothermal compressibility (Table 2). This assumption does not influence on the final calculations of the Kirkwood–Buff integrals [68,69]. The resulting equations for G_{ij} are given elsewhere [44,68]. Using the G_{ij} quantities, it is possible to estimate the so-called linear coefficients of preferential solvation, δ_{ij}^0 [68] (e.g., $\delta_{12}^0 = x_1 x_2 (G_{12} - G_{22})$) which are useful quantities to determine the local mole fractions of the i species around the central j molecule [68,69]

$$x_{ij} = x_i + \frac{\delta_{ij}^0}{V_c} \tag{12}$$

where V_c is the volume for solvation sphere. This value may be roughly estimated [69] as the volume of a sphere of radius $R_c = 3r$, where r is the radius of the central molecule. This leads to a value of V_c equal to approximately $(3^2 - 1)\, V_c = 26V_0$, being V_0 the molar volume of the solvated component [69].

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 [70]. Final values of the fitted parameters in this work are collected in Table 3. Some important remarks are given below.

3.1.1. Amine + aromatic compound, or + alkane systems

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

(a) For the sake of simplicity, in systems with aromatic hydrocarbons, no distinction is made between the aromatic surface in the hydrocarbon and in the amine.
(b) The (a,b) contacts are represented by DIS parameters only, which are known from experimental data for 1,3-dimethylbenzene, or 1,3,5-trimethylbenzene + alkane systems [71], as these aromatic hydrocarbons are homomorphic with the pyridine bases considered (2,4-; 2,6-; 3,5-dimethylpyridine and 1,3,5-trimethylpyridine).
(c) The (b,n) contacts are assumed to be represented by DIS parameters only. The same choice was selected for the pyridine, or methylpyridine + benzene, or + toluene [59] mixtures due to the low H^E values of such solutions: 8 J mol^{-1} at equimolar composition and 298.15 K for the pyridine + benzene system [72]. In addition, this solution

Table 2

Physical constants at 298.15 K of pure compounds needed for the application of the Flory theory or the Kirkwood–Buff formalism: coefficients of thermal expansion, α, isothermal compressibility, κ_T, and reduction parameters, V_i^* and P_i^*

Compound	α (10^{-3} K)	κ_T (10^{-12} Pa^{-1})	V_i^* (cm^3 mol^{-1})	P_i^* (J cm^{-3})
Pyridine	1.070[a]	699.6[b]	64.08	726.1
2-Methylpyridine	0.989[a]	753.4[b]	79.58	607.1
3-Methylpyridine	0.969[a]	710[c]	78.82	639.9
4-Methylpyridine	0.965[a]	691.9[c]	79.0	383.4
2,4-Dimethylpyridine	0.841[a]	964[d]	95.26	541.2
2,6-Dimethylpyridine	0.982[a]	1053[e]	93.83	589.2
3,5-Dimethylpyridine	0.898[f]	964[d]	92.23	602.8
2,4,6-Trimethylpyridine	0.988[b]	1059[g]	106.65	598.6
Heptane	1.256[h]	1460.6[h]	113.4	431.9
Methanol[i]	1.196[a]	1248[a]		

[a] [103].
[b] [80].
[c] [106].
[d] From adiabatic compressibilities measurements [107] using heat capacities from [108].
[e] From adiabatic compressibilities measurements [109] using heat capacities from [108].
[f] [84].
[g] From adiabatic compressibilities measurements [110] using heat capacities from [108].
[h] [111] $V = 147.45$ cm^3 mol^{-1} [103].
[i] $V = 40.75$ cm^3 mol^{-1} [103].

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]	$C^{DIS}_{sn,1}$	$C^{DIS}_{sn,2}$	$C^{DIS}_{sn,3}$	$C^{QUAC}_{sn,1}$	$C^{QUAC}_{sn,2}$	$C^{QUAC}_{sn,3}$
2,4-Dimethylpyridine + $CH_3(CH_2)_nCH_3$	(a,n)	9.05	19.4	36	7	7	−20
2,4-Dimethylpyridine + aromatic compound	(b,n)	10.45	15	26			
2,6-Dimethylpyridine + $CH_3(CH_2)_nCH_3$	(a,n)	9.05	19.4	36	7	5.5	−20
2,6-Dimethylpyridine + aromatic compound	(b,n)	10.45	15	26			
3,5-Dimethylpyridine + $CH_3(CH_2)_nCH_3$	(a,n)	15	24.2	36	7	10.5	−20
3,5-Dimethylpyridine + aromatic compound	(b,n)	14.9	21	26			
2,4,6-Trimethylpyridine + $CH_3(CH_2)_nCH_3$	(a,n)	9.05	30	36	7	3	−20
2,4,6-Trimethylpyridine + aromatic compound	(b,n)	10.45	21.5	26			
2,6-Dimethylpyridine + methanol	(h,n)	−19	−44.4	10	−3.9	−1.9	−5
2,6-Dimethylpyridine + ethanol	(h,n)	−13.8	−50[b]	10	−3.5	1[b]	−5
2,6-Dimethylpyridine + 1-propanol	(h,n)	−18	−50[b]	10	−3.5	1[b]	−5
2,6-Dimethylpyridine + ≥1-butanol	(h,n)	−20.8	−50[b]	10	−3.5	1[b]	−5
2,4,6-Trimethylpyridine + methanol	(h,n)	−21[b]	−41.3[b]	10	−3.9	−1.9	−5
2,4,6-Trimethylpyridine + ethanol	(h,n)	−16[b]	−50[b]	10	−3.5	−1.2[b]	−5
2,4,6-Trimethylpyridine + 1-propanol	(h,n)	−19[b]	−50[b]	10	−3.5	−1.2[b]	−5
2,4,6-Trimethylpyridine + ≥1-butanol	(h,n)	−23[b]	−50[b]	10	−3.5	−1.2[b]	−5

[a] s = a, CH_3 or CH_2 in alkanes, alkyl derivatives of benzene or pyridine, and in 1-alkanols; s = b, b, aromatic ring in the pyridine bases studied (C_5H_3 or C_5H_2) or in benzene and in its alkyl derivatives; s = h, OH in 1-alkanols; s = n, N in pyridine bases.

[b] Estimated values.

also shows a slightly positive C_P^E [72], a characteristic of systems where dipolar or dipole-induced dipole interactions are present [29]. A similar behaviour is expected for the actual mixtures with aromatic hydrocarbons, which is supported by the values of their thermodynamic properties [73].

(d) The $C^{QUAC}_{an,l}$(l = 1, 3) interchange coefficients are considered to be the same than those of mixtures with pyridine or methylpyridines. The same occurs in many different systems previously investigated (see [29] and references herein).

3.1.2. Amine + 1-alkanol systems

These solutions are characterized by the following contacts: (a,b); (a,h); (a,n); (b,h); (n,b); and (h,n). The (a,h) contacts in 1-alkanol + alkane mixtures are described by DIS and QUAC interaction parameters [26,74]. Similarly it occurs for the (b,h) contacts in 1-alkanol + 1,3-dimethylbenzene, or 1,3,5-trimethylbenzene systems [75]. Therefore, only the $C^{DIS/QUAC}_{nh,l}$coefficients must be determined as the remainder parameters are already known.

3.2. FLORY interaction parameters

Here, calculations were developed using the expression, reported recently by us, which makes possible to determine χ_{12} from H^E at a given composition [35]. Such expression generalizes that previously given to obtain χ_{12} directly from H^E at equimolar composition [76]. Values of the reduction parameters P_i^*, V_i^* ($i = 1, 2$) for pure compounds needed for the calculations are listed in Table 2. In order to obtain detailed information on the concentration dependence of χ_{12}, we have calculated this magnitude from smoothed H^E values at $x_1 = 0.05$ in the composition range [0.05, 0.95]. Results are shown in graphical way in Fig. 1.

4. Results

Results from the DISQUAC model are compared with experimental data for VLE, G^E, H^E, $S_{CC}(0)$ and x_{ij} in Tables 4–7. Comparisons for selected mixtures are plotted in Figs. 2–5.

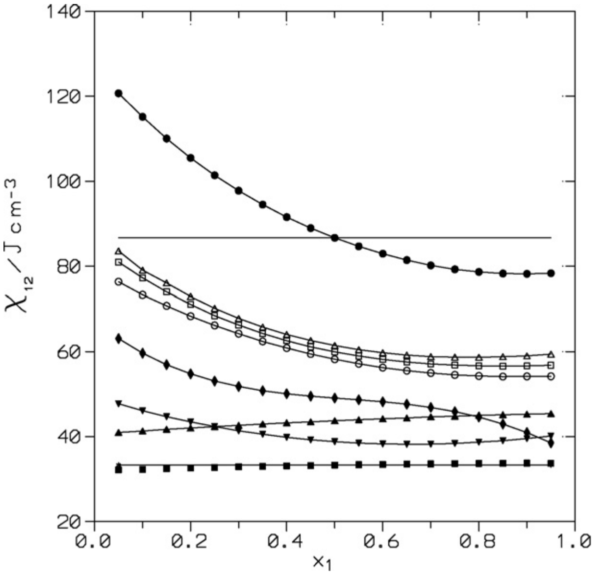

Fig. 1. $\chi_{12}(x_1)$ energetic parameter of the Flory theory for pyridine base (1) + heptane(2) mixtures at temperature T: (●), pyridine; (○), 2-methylpyridine; (□), 3-methylpyridine; (△), 4-methylpyridine; (▲), 2,4-dimethylpyridine; (■),2,4,6-trimethylpyridine (T = 298.15 K); (▼), 2,6-dimethylpyridine; (♦), 3,5-dimethylpyridine (T = 303.15 K). Straight lines, χ_{12} parameter at equimolar composition for systems with pyridine or 2,4,6-trimethylpyridine.

Table 4
Molar excess Gibbs energies, G^E, at equimolar composition and temperature T, for pyridine base (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]	
2,4-Dimethylpyridine(1) + organic solvent(2)									
1,2-Dimethylbenzene	373.15	12	88	65		0.001	0.006		[112]
2,6-Dimethylpyridine(1) + organic solvent(2)									
1,2-Dimethylbenzene	373.15	12	63	65		0.0006	0.0009		[112]
1,3-Dimethylbenzene	373.15	12	70	65		0.0004	0.001		[112]
1,4-Dimethylbenzene	373.15	11	75	65		0.0003	0.001		[112]
Hexane	263.15	8	652	650	396	0.005	0.040	0.210	[84]
	298.15	8	601	613	377	0.002	0.030	0.150	[84]
	353.15	8	525	550	368	0.003	0.027	0.079	[84]
Heptane	263.15	9	645	691	373	0.004	0.033	0.16	[84]
	298.15	9	564	650	344	0.004	0.052	0.10	[84]
	353.15	9	453	583	324	0.006	0.063	0.046	[84]
Octane	263.15	8	651	719	352	0.007	0.048	0.13	[84]
	298.15	8	582	674	315	0.004	0.044	0.097	[84]
	353.15	8	461	601	284	0.003	0.048	0.053	[84]
Methanol	298.15	10	−288	−285	670	0.006	0.036	0.810	[91]
	313.15	19	−219	−219	742	0.004	0.038	0.720	[113]
	318.15	10	−191	−197	756	0.003	0.033	0.680	[91]
Ethanol	313.15	12	−56	−54	503	0.001	0.009	0.290	[113]
1-Propanol	313.15	16	−201	−201	351	0.002	0.004	0.230	[113]
1-Butanol	313.15	15	−271	−275	234	0.002	0.008	0.150	[113]
3,5-Dimethylpyridine(1) + organic solvent(2)									
Hexane	273.15	7	718	782	593	0.005	0.24	0.071	[84]
	298.15	7	696	752	550	0.004	0.22	0.075	[84]
	333.15	7	639	702	528	0.007	0.19	0.050	[84]
Heptane	273.15	7	827	832	544	0.007	0.017	0.140	[84]
	298.15	7	819	798	489	0.008	0.027	0.110	[84]
	343.15	7	725	726	446	0.008	0.021	0.110	[84]
Octane	273.15	7	870	867	501	0.010	0.018	0.220	[84]
	298.15	7	939	829	436	0.013	0.089	0.270	[84]
	343.15	7	763	750	383	0.011	0.030	0.160	[84]
2,4,6-Trimethylpyridine(1) + organic solvent(2)									
1,2,4-Trimethylbenzene	373.15	12	59	47		0.001	0.003		[114]
1,3,5-Trimethylbenzene	373.15	12	56	47		0.0006	0.002		[114]

[a] Number of data points.
[b] Eq. (13).
[c] Experimental result.
[d] DISQUAC values calculated with interaction parameters from Table 2.
[e] UNIFAC values calculated with interaction parameters from the literature [23,65].

Fig. 6 shows DISQUAC calculations for G_{ij} of the 2,4,6-trimethylpyridine + heptane mixture at 298.15 K. For the sake of clarity, relative deviations for the pressure (P) and H^E defined as

$$\sigma_r(P) = \left\{ \frac{1}{N} \sum \left[\frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{exp}}} \right]^2 \right\}^{1/2} \tag{13}$$

and

$$\text{dev}(H^E) = \left\{ \frac{1}{N} \sum \left[\frac{H^E_{\text{exp}} - H^E_{\text{calc}}}{|H^E_{\text{exp}}(x_1 = 0.5)|} \right]^2 \right\}^{1/2} \tag{14}$$

are given in Tables 4 and 5, 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. The large $\sigma_r(P)$ values for 3,5-dimethylpyridine + hexane system (Table 4) are due to the poor results provided by the model at very high x_1 values for this mixture.

DISQUAC improves the theoretical calculations from UNIFAC (Tables 4 and 5). The poor results obtained using UNIFAC merely underline that the investigated amines should not be treated as a homologous series, and indicate that each pyridine base should be characterized by its own interaction parameters.

5. Discussion

Hereafter, we are referring to values of the thermodynamic properties at equimolar composition and 298.15 K. H^E (Table 5) and V^E [77–80] of the dimethyl or trimethylpyridine + alkane mixtures are usually positive and increase with the chain length of the alkane. Therefore, the main contribution to these excess functions comes from the disruption of the amine–amine inter-

Table 5
Molar excess enthalpies energies, H^E, at equimolar composition and temperature T, for pyridine base(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]	
2,4-Dimethylpyridine(1) + organic solvent(2)									
Benzene	298.15		81	19					[73]
1,2-Dimethylbenzene	298.15		88	112					[115]
Hexane	298.15		951	1016	844	0.006	0.092	0.097	[86]
Heptane	298.15		1047	1090	909	0.004	0.053	0.169	[86]
Octane	298.15		1166	1156	967	0.004	0.035	0.138	[86]
Nonane	298.15		1230	1216	1019	0.004	0.012	0.148	[86]
Decane	298.15		1281	1271	1066	0.003	0.009	0.138	[86]
2,6-Dimethylpyridine(1) + organic solvent(2)									
Benzene	298.15		76	49	74				[73]
			71						[72]
	313.15		59	48	97				[72]
	333.15		41	50	133				[72]
1,2-Dimethylbenzene	373.15		90	112					[115]
Hexane	303.15		940	950	496	0.012	0.018	0.400	[84]
Heptane	303.15		1000	1017	501	0.013	0.015	0.389	[84]
Octane	303.15		1059	1076	573	0.013	0.035	0.388	[84]
Methanol	298.15		−1639	−1635	−164	0.011	0.030	0.689	[81]
3,5-Dimethylpyridine(1) + organic solvent(2)									
Benzene	298.15		33	48					[72]
	333.15		23	28					[72]
Toluene	303.15		108	41					
Hexane	303.15		1162	1163	796	0.008	0.013	0.266	[84]
Heptane	303.15		1235	1251	837	0.009	0.023	0.283	[84]
Octane	303.15		1276	1331	871	0.005	0.039	0.273	[84]
2,4,6-Trimethylpyridine(1) + organic solvent(2)									
1,2-Dimethylbenzene	298.15		21	18					[115]
Hexane	298.15		781	852	423	0.003	0.059	0.396	[87]
Heptane	298.15		934	913	457	0.004	0.025	0.403	[87]
Octane	298.15		970	967	487	0.003	0.011	0.405	[87]
Nonane	298.15		1016	1015	514	0.004	0.014	0.399	[87]
Decane	298.15		1040	1059	539	0.008	0.025	0.400	[87]
Methanol	303.15		−1555	−1479		0.011	0.055		[116]
1-Propanol	313.15		−894	−930		0.007	0.123		[117]
1-Butanol	313.15		−789	−782		0.020	0.090		[117]
1-Pentanol	313.15								[117]
1-Hexanol	313.15		−667	−552		0.014	0.114		[117]

[a] Number of data points.
[b] Eq. (14).
[c] Experimental result.
[d] DISQUAC values calculated with interaction parameters from Table 2.
[e] UNIFAC values calculated with interaction parameters from the literature [23,65].

actions. The large $S_{CC}(0)$ values (>0.25) (Table 6) show the rather strong homocoordination characteristic of these systems. In agreement with this fact, $G_{ii} > 0$ and $G_{12} < 0$ (Fig. 6), indicating that interactions between like molecules are predominant over those of type 1 and 2. Structural effects are present in solutions with the shorter alkanes, as the S-shaped V^E curves reveal [77–80].

Mixtures containing aromatic hydrocarbons are nearly ideal. This is supported by low positive H^E values (Table 5) and $S_{CC}(0)$ values which are close to 0.25 (Table 6). In addition, DISQUAC calculations show that $S_{CC}(0)$ weakly depends on the temperature, which points out to the great stability of these systems.

The large and negative H^E (−1639 J mol^{-1}) of the methanol + 2,6-dimethylpyridine mixture [81] (Fig. 5) reveals the importance of the amine–alcohol interactions in the corresponding alcoholic solutions. This is consistent with $S_{CC}(0) < 0.25$ (Table 6). It is necessary to remark here that size effects are responsible in part of the heterocoordination present in systems with methanol, as it is shown by the large combinatorial contribution to $S_{CC}(0)^{-1}$ (Table 6).

5.1. The effect of increasing the number of methyl groups attached to the aromatic ring

5.1.1. Mixtures with alkanes

This effect leads to a decreasing of H^E and V^E. In mixtures with heptane, we observe that H^E varies as follows (all values in J mol^{-1}): 1735 (pyridine) [82] > 1371 (3-methylpyridine)

Table 6
Concentration–concentration structure factor, $S_{CC}(0)$, at temperature T and equimolar composition for pyridine(1) base(1) + organic solvent(2) mixtures

System	T (K)	$S_{CC}(0)$		$S_{CC}(0)^{-1}$		Ref.
		Exp.[a]	DQ[b]	Comb[c]	Int.[d]	
Pyridine + n-C_7	298.15	1.09	1.22	0.302	−3.48	[118]
	313.15	1.01	0.96		−3.26	[119]
Pyridine + n-C_8	313.15	1.07	0.84	0.437	−3.25	[119]
Pyridine + n-C_9	313.15	0.92	0.77	0.572	−3.27	[119]
2-Methylpyridine + n-C_7	313.15	0.58	0.58	0.114	−2.34	[119]
2-Methylpyridine + n-C_8	313.15	0.61	0.58	0.208	−2.47	[119]
2-Methylpyridine + n-C_9	313.15	0.54	0.57	0.311	−2.55	[119]
3,5-Dimethylpyridine + n-C_6	273.15	0.90	0.71	0.0004	−2.59	[84]
	298.15	0.69	0.59		−2.31	[84]
	343.15	0.56	0.46		−1.85	[84]
3,5-Dimethylpyridine + n-C_7	273.15	1.00	0.81	0.025	−2.79	[84]
	298.15	0.85	0.65		−2.48	[84]
	343.15	0.62	0.47		−1.89	[84]
3,5-Dimethylpyridine + n-C_8	273.15	0.75	0.88	0.078	−2.95	[84]
	298.15	0.60	0.68		−2.62	[84]
	343.15	0.43	0.50		−2.09	[84]
2,6-Dimethylpyridine + n-C_6	263.15	0.56	0.56	0.0004	−2.22	[84]
	298.15	0.47	0.47		−1.86	[84]
	343.15	0.39	0.40		−3.69	[84]
2,6-Dimethylpyridine + n-C_7	263.15	0.56	0.61	0.025	−2.40	[84]
	298.15	0.46	0.50		−2.01	[84]
	343.15	0.39	0.41		−1.60	[84]
2,6-Dimethylpyridine + n-C_8	263.15	0.52	0.65	0.078	−2.54	[84]
	298.15	0.41	0.51		−2.13	[84]
	343.15	0.33	0.42		−1.71	[84]
2,4-Dimethylpyridine + 1,2-dimethylbenzene	298.15		0.27	0.003	−0.26	
	373.15	0.26	0.26		−0.17	[112]
2,6-Dimethylpyridine + benzene	298.15		0.26	0.104	−0.20	
	373.15		0.25		−0.18	[112]
2,6-Dimethylpyridine + 1,2-dimethylbenzene	298.15		0.27		−0.26	
	373.15	0.26	0.26	0.003	−0.17	[112]
2,6-Dimethylpyridine + 1,3-dimethylbenzene	373.15	0.26	0.26	0.003	−0.17	[112]
2,6-Dimethylpyridine + 1,4-dimethylbenzene	373.15	0.26	0.26	0.003	−0.17	[112]
2,4,6-Trimethylpyridine + 1,2,4-trimethylbenzene	373.15	0.26	0.26	0.002	−0.124	[114]
2,4,6-Trimethylpyridine + 1,3,5-trimethylbenzene	373.15	0.26	0.26	0.002	−0.124	[114]
Methanol + pyridine	298.15	0.224	0.235	0.477	−0.22	
	313.15	0.233	0.241		−0.32	[113]
Methanol + 2-methylpyridine	298.15	0.200	0.220	0.773	−0.24	
	313.15	0.210	0.228		−0.40	[113]
Methanol + 2,6-dimethylpyridine	298.15	0.19	0.22	1.04	−0.54	[91]
	313.15	0.20	0.23		−0.72	[113]
	318.15	0.20	0.23		−0.78	[91]
Ethanol + 2,6-dimethylpyridine	313.15	0.24	0.25	0.5	−0.48	[113]
1-Propanol + 2,6-dimethylpyridine	313.15	0.22	0.22	0.21	0.30	[113]
1-Butanol + 2,6-dimethylpyridine	313.15	0.21	0.21	0.06	0.70	[113]

[a] Exprerimental results.
[b] DISQUAC calculations interaction parameters from Table 2.

[c] Combinatorial contribution to $S_{cc}(0)^{-1}$.
[d] Interactional contribution to $S_{cc}(0)^{-1}$ using DISQUAC.

[83] > 1235 (3,5-dimethylpyridine, T = 303.15 K) [84] and pyridine > 1346 (2-methylpyridine) [85] > 1047 (2,4-dimethylpyridine) [86] > 934 (2,4,6-trimethylpyridine) [87]. Such H^E variations can be ascribed to a weakening of the orientational effects in the same sequences. Note that $\bar{\mu}$ and ΔT_b also decrease usually with the number of CH_3 groups attached to the aromatic ring. As a matter of fact, for a pure polar liquid, the potential energy related to dipole–dipole interactions is in first approximation given by $-(\bar{\mu})^4/r^6$ [88] or more roughly by $-(\bar{\mu})^4/V^2$ [89], where r is the distance between dipoles. So, the decrease of the dipolar interactions is the aforementioned. In terms of the DISQUAC model, this behaviour is represented by a $H^{E,DIS}/H^{E,QUAC}$ ratio which varies in opposite way to H^E: 1.01 (pyridine) < 1.09 (3-methylpyridine) < 1.33 (3,5-dimethylpyridine) and 1.01 (pyridine) ≈ 0.99 (2-methylpyridine) < 2.09 (2,4-dimethylpyridine) <5.76 (2,4,6-

Table 7
Local molar fractions, x_{ij}, of methanol(1) + pyridine base(2) mixtures at 298.15 K and composition x_1, calculated according to the Kirkwood–Buff theory using VLE and V^E data from [91]

Pyridine base	x_1	x_{11}		x_{22}		x_{12}	
		Exp.[a]	DQ.[b]	Exp.[a]	DQ.[b]	Exp.[a]	DQ.[b]
Pyridine	0.2	0.208	0.209	0.797	0.797	0.202	0.203
	0.4	0.406	0.408	0.595	0.595	0.405	0.405
	0.5	0.506	0.507	0.494	0.495	0.506	0.505
	0.6	0.606	0.606	0.394	0.394	0.606	0.606
	0.8	0.805	0.804	0.196	0.195	0.804	0.805
2-Methylpyridine	0.2	0.208	0.206	0.796	0.796	0.204	0.204
	0.4	0.404	0.409	0.593	0.594	0.406	0.406
	0.5	0.505	0.508	0.493	0.493	0.507	0.506
	0.6	0.605	0.607	0.393	0.393	0.607	0.607
	0.8	0.806	0.804	0.195	0.193	0.805	0.806
2,6-Dimethylpyridine	0.2	0.209	0.204	0.796	0.796	0.204	0.204
	0.4	0.404	0.413	0.593	0.593	0.407	0.406
	0.5	0.505	0.512	0.492	0.493	0.508	0.507
	0.6	0.607	0.609	0.392	0.393	0.608	0.607
	0.8	0.809	0.805	0.195	0.193	0.805	0.807

[a] Experimental result.
[b] DISQUAC calculation using the interaction parameters from Table 2.

trimethylpyridine). On the other hand, from the study of the $\chi_{12}(x_1)$ function (Fig. 1), it is possible to conclude that orientational effects become weaker in the order: pyridine > methylpyridine > dimethylpyridine > trimethylpyridine. It is remarkable that for the latter system, $\chi_{12}(x_1)$ is nearly constant, which is in agreement with the much larger DIS contribution to H^E in terms of DISQUAC. The mentioned weakening of the orientational effects also explains, at least in part, the V^E variation: V^E (pyridine + heptane) = 0.2657 [60] > V^E (2-methylpyridine + heptane) = 0.1977 [90] > V^E (2,4-dimethylpyridine + heptane) = 0.117 [79] (values in $cm^3\ mol^{-1}$).

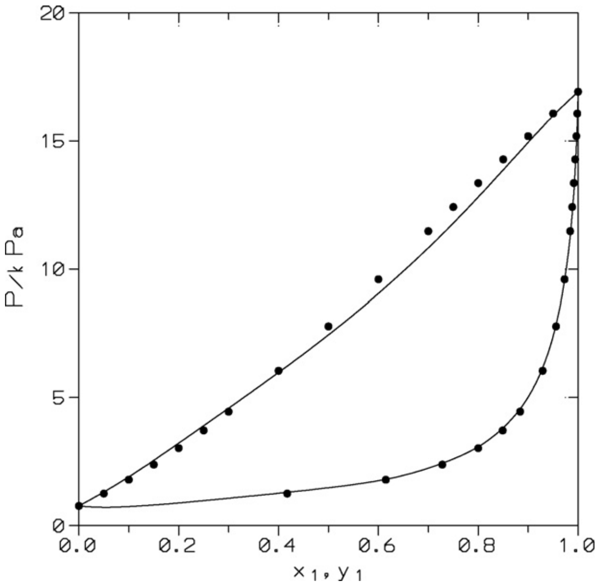

Fig. 2. VLE for the methanol(1) + 2,6-dimethylpyridine(2) system at 298.15 K. Points, experimental results [91]. Solid lines, DISQUAC calculations.

$S_{CC}(0)$ results (Table 6) show that homocoordination decreases in the order: pyridine > 3,5-dimethylpyridine and pyridine > 2-methylpyridine > 2,6-dimethylpyridine. This behaviour may be ascribed to the steric hindrances, exerted by the CH_3– groups in the pyridine base when creating the amine–amine interactions, increase with the number of these groups.

5.1.2. Mixtures with 1-alkanols

We note that for systems with methanol, both H^E and V^E decrease in the same order than in systems with a given alkane. In the case of V^E: −0.483 (pyridine) > −0.958 (2-

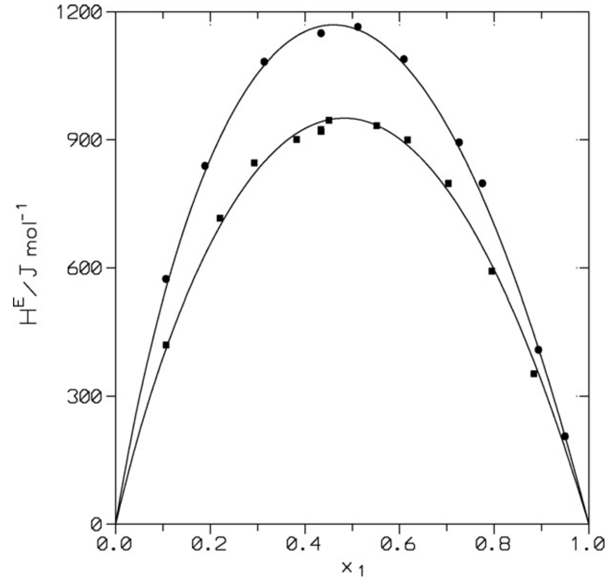

Fig. 3. H^E at 303.15 K for dimethylpyridine(1) + hexane(2) systems. Points, experimental results [84]: (●), 3,5-dimethylpyridine; (■), 2,6-dimethylpyridine. Solid lines, DISQUAC calculations.

Table 8
Partial excess molar enthalpies, $H_1^{E,\infty}$, at 298.15 K for solute(1) + organic solvent(2) mixtures and hydrogen bond interaction energy, $\Delta H_{(OH–N)H\text{-bond}}$, for methanol(1) + pyridine base(2) systems

System	$H_1^{E,\infty}$/kJ mol^{-1}	$\Delta H_{(OH–N)H\text{-bond}}$	Ref.
Pyridine + heptane	8.73		[82]
2-Methylpyridine + heptane	6.61		[85]
2,6-Dimethylpyridine + heptane	4.83[a]		[84]
2,4,6-Trimethylpyridine + heptane	3.3		[87]
Methanol + heptane	25.1		[36,38]
Methanol + pyridine	−1.67	−35.5	[81]
Methanol + 2-methylpyridine	−3.60	−35.3	[81]
Methanol + 2,6-dimethylpyridine	−5.46	−35.3	[81]
Methanol + 2,4,6-trimethylpyridine	−6.2[a]	−34.6	[116]

[a] Value at 303.15 K.

methylpyridine) > −1.503 (2,6-dimethylpyridine) (values in cm^3 mol^{-1}) [91], and for H^E: −711 (pyridine) > −1261 (2-methylpyridine) > −1635 (2,6-dimethylpyridine) [81] (values in J mol^{-1}). This variation can be explained taking into consideration the lower positive contribution to H^E from the disruption of the amine–amine interactions when the size of the amine increases. The fact that the energies of the OH···N hydrogen bonds are practically independent of the pyridine base considered (Table 8) supports this conclusion. A previous estimation of the hydrogen-bond energy variation with the acidity constant and with the ionization energy indicates that the OH···N hydrogen bonds are not hindered by steric effect of methyl substitution [81]. The mentioned energies can be estimated as follows. H^E can be written as

$$H^E = \Delta H_{OH–OH} + \Delta H_{N–N} + \Delta H_{OH–N} \tag{15}$$

This type of equation has been rather widely used [92–94]. It can be extended to $x_1 \to 0$ [95] to evaluate $\Delta H_{(OH–N)bond}$, the strength of the H-bonds between molecules of 1-alkanol and a pyridine base in the studied solutions. In such case, $\Delta H_{(OH–OH)}$ and $\Delta H_{(N–N)}$ can be replaced by $H_1^{E,\infty}$ (partial excess molar enthalpy at infinite dilution of the first component) of 1-alkanol or pyridine base + heptane systems. So

$$\begin{aligned}\Delta H_{(OH–N)H\text{-bond}} = {} & H_1^{E,\infty}(1-\text{alkanol} + \text{pyridine base}) \\ & - H_1^{E,\infty}(1-\text{alkanol} + n - \text{C}_7) \\ & - H_1^{E,\infty}(\text{pyridine base} + n - \text{C}_7)\end{aligned} \tag{16}$$

This is a rough estimation of $\Delta H_{(OH–N)H\text{-bond}}$ as some of the $H_1^{E,\infty}$ (Table 8) data used were calculated from H^E measurements over the entire mole fraction range. For the methanol + heptane system, it was considered that $H_1^{E,\infty}$ = 25.1 kJ mol^{-1}, in agreement with the values of the hydrogen bond energies for 1-alkanols used in the ERAS model (−25.1 kJ mol^{-1} for all the 1-alkanols) [36,38]. The $\Delta H_{(OH–N)H\text{-bond}}$ value obtained (≈−35.2 kJ mol^{-1}, Table 8) fits well into the general scheme of the 1-alkanol + amine mixtures when are examined in terms of the ERAS model. So, the ener-

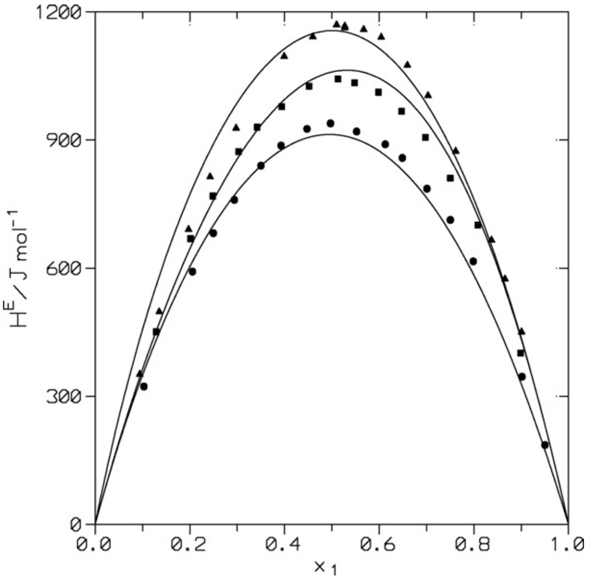

Fig. 4. H^E at 298.15 K for pyridine base(1) + alkane(2) systems. Points, experimental results: (▲), 2,4-dimethylpyridine(1) + octane(2) [86]; (●), 2,4,6-trimethylpyridine(1) + hexane(2); (■), 2,4,6-trimethylpyridine(1) + decane (2) [87]. Solid lines, DISQUAC calculations.

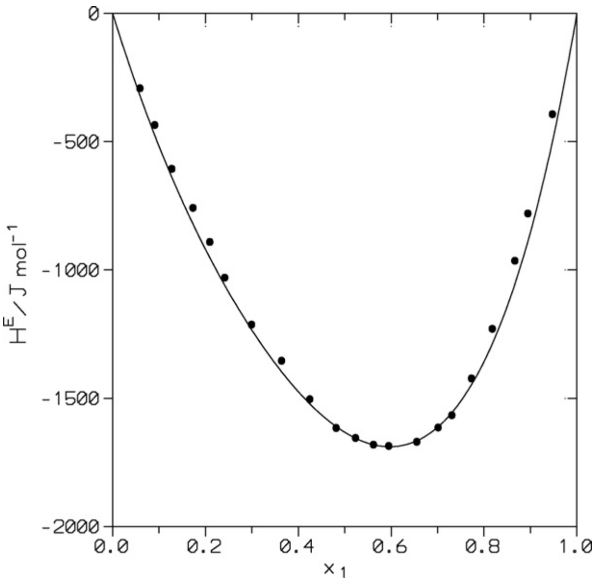

Fig. 5. H^E at 298.15 K for methanol(1) + 2,6-dimethylpyridine(2) system. Points, experimental results [81]. Solid lines, DISQUAC calculations.

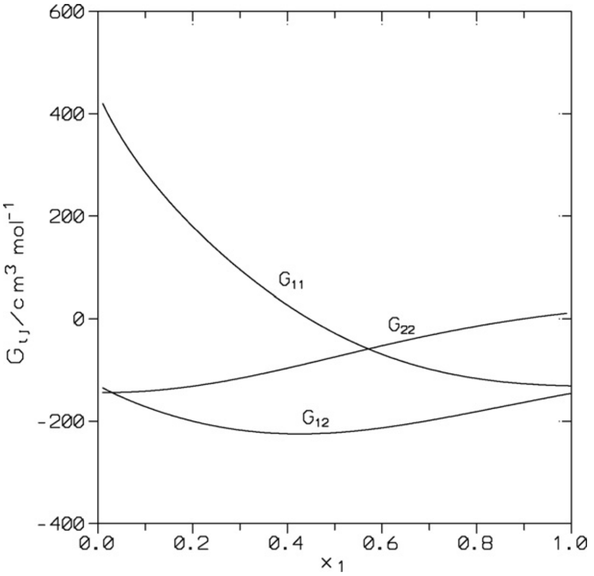

Fig. 6. G_{ij} for the 2,4,6-trimethylpyridine (1) + heptane(2) mixture at 298.15 K. Results using the DISQUAC model and V^E from [78].

gies of the OH$\cdots$N bonds for methanol + amine mixtures are: -42.4 kJ mol^{-1} for hexylamine [96]; dipropylamine [97] or dibutylamine [98] and -35.3 kJ mol^{-1} for *N,N,N*-triethylamine [96], respectively.

For methanol systems, $S_{CC}(0)$ also changes in the sequence pyridine > 2-methylpyridine > 2,6-dimethylpyridine (Table 6). This seems to indicate that size effects are predominant over steric hindrances to the creation of the OH$\cdots$N hydrogen bonds, which are expected to increase with the number of methyl groups in the pyridine base. Note that the combinatorial contribution to $S_{CC}(0)^{-1}$ increases with the size of the amine (Table 6). The importance of the size effects can be also investigated by analysing the contribution to the H^E from the so-called equation of state term, which neglecting terms of higher order in V^E, is displayed to a good approximation by [2,99] $-\alpha T V^E/\kappa_T$ where α and κ_T are the isobaric expansion coefficient and the isothermal compressibility factor of the mixture, respectively. Due to the lack of experimental data, these quantities were calculated as $M = \Phi_1 M_1 + \Phi_1 M_2$, where M is the value of α or κ_T for the mixture, and M_i, the value of these magnitudes for the pure compounds ($i = 1$, 2) (see Table 2). Using V^E data from [91], we obtain for the mentioned equation of state contribution to H^E the values: -181, -334 and -523 J mol^{-1} for the solutions with pyridine, 2-methylpyridine or 2,6-dimethylpyridine, respectively.

It is interesting to investigate now the mixture structure by calculating the local mole fractions x_{ij} from the Kirkwood–Buff theory (Table 7) using V^E data from [91]. We note that the local mole fractions are close to the bulk ones. A possible interpretation is based on the assumption that these mixtures are approximately random, in contrast with their low and negative H^E values, which reveal strong intermolecular interactions in the solution (see above). It is then possible to conclude that intermolecular interactions between molecules lead essentially to orientational effects within the solvation shell. The same behaviour has been found in amide + 1-alkanol mixtures [100–102].

5.2. *The effect of modifying the position of the methyl groups attached to the aromatic ring*

Here, we are focusing our attention to mixtures with heptane. H^E changes in the sequence: 1235 (3,5-dimethylpyridine, $T = 303.15$ K) [84] > 1047 (2,4-dimethylpyridine) [86] > 1000 (2,6-dimethylpyridine, $T = 303.15$ K) [84], in agreement with the relative variations of the $\bar{\mu}$ and ΔT_b (Table 1). A similar trend is also observed in systems with methylpyridines [59]. However, V^E varies is opposite way: V^E (2,4-dimethylpyridine) = 0.117 [79] < V^E (2,6-dimethylpyridine) = 0.1847 [77] cm^3 mol^{-1}. This may be attributed to packing effects as the different values of the molar volumes of these dimethylpyridines indicate (Table 1). On the other hand, homocoordination is higher in solutions with 3,5-dimethylpyridine than in those with 2,6-dimethylpyridine, which is supported by our $S_{CC}(0)$ results (Table 6). This suggests that the steric effects exerted by methyl groups in positions 2 and 6 are higher than when they are placed in positions 3 and 5.

5.3. *The DISQUAC interaction parameters*

It is known that the interchange energy is defined by $\Delta\varepsilon_{st} = \varepsilon_{st} - (\varepsilon_{ss} + \varepsilon_{tt})/2$, where ε_{st}, ε_{ss}, ε_{tt} represent the interaction energies between the surfaces *s–t*, *s–s* and *t–t* and have negative values. In the framework of DISQUAC, $\varepsilon_{st} = g_{st}$, h_{st}. The QUAC parameters are more related to orientational effects, while the DIS parameters are related to non-specific interactions. We note that the $C^{QUAC}_{an,2}$ coefficients decrease as follows: 3,5-dimethylpyridine > 2,4-dimethylpyridine > 2,6-dimethylpyridine (Table 3). This may be interpreted assuming that orientational effects become weaker in the same order (see above), and also explains the observed decrease of the $C^{QUAC}_{an,2}$ coefficients when the number of methyl groups in the pyridine base increases: $C^{QUAC}_{an,2}$(pyridine) = 14.1 [59] > $C^{QUAC}_{an,2}$ (2-methylpyridine) = 12 [59] > $C^{QUAC}_{an,2}$ (2,4-dimethylpyridine) = 5.5 > $C^{QUAC}_{an,2}$ (2,4,6-trimethylpyridne) = 3. For mixtures with 1-alkanols, the important point is that the $|C^{DIS}_{hn,2}|$ values are much higher than those of $|C^{QUAC}_{hn,2}|$, which points out that non-specific effects are predominant, in agreement with the findings encountered on the basis of the Kirkwood–Buff formalism.

6. Conclusions

Mixtures with dimethyl or trimethylpyridines and alkane, aromatic compound or 1-alkanol have been characterized in terms of DISQUAC. H^E and V^E decrease in systems with alkane or methanol in the order: pyridine > 3-methylpyridine > 3,5-dimethylpyridine and pyridine > 2-methylpyridine > 2,4-dimethylpyridine > 2,4,6-trimethylpyridine, which has been attributed to a weakening of the amine–amine interactions in the same sequences. This is in agreement with the relative variation of $\bar{\mu}$ and ΔH_b, and supports that for heptane solutions H^E (3,5-dimethylpyridine) > H^E (2,4-dimethylpyridine) > H^E (2,6-dimethylpyridine). Calculations on the basis of the Flory model confirm that orientational effects become weaker in systems with alkane in the order: pyridine > methylpyridine > dimethylpyridine > trimethylpyridine. $S_{CC}(0)$ calculations show that steric effects increase with the number of CH_3– groups in the pyridine base, and that steric effects exerted by methyl groups in positions 2 and 6 are higher that when they are placed in positions 3 and 5. The hydrogen bond energy in methanol mixtures is independent of the pyridine base. Heterocoordination in these solutions is due in part to size effects. Their structure is nearly random. The values of the local mole fractions calculated from the Kirkwood–Buff theory support this conclusion as they are close to the bulk ones.

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