Thermodynamics of mixtures containing amines. IX. Application of the concentration–concentration structure factor to the study of binary mixtures containing pyridines

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ABSTRACT

Binary mixtures formed by a pyridine base and an alkane, or an aromatic hydrocarbon, or a 1-alkanol have been studied in the framework of the concentration–concentration structure factor, $S_{CC}(0)$, formalism. Deviations between experimental data and those provided by the DISQUAC model are discussed. Systems containing alkanes are characterized by homocoordination. In pyridine + alkane mixtures, $S_{CC}(0)$ decreases with the chain length of the longer alkanes, due to size effects. For a given alkane, $S_{CC}(0)$ also decreases with the number of $CH_3–$ groups in the pyridine base. This has been interpreted assuming that the number of amine–amine interactions available to be broken upon mixing also decreases similarly, probably as steric hindrances exerted by the methyl groups of the aromatic amine increase with the number of these groups. Homocoordination is higher in mixtures with 3,5-dimethylpyridine than in those with 2,6-dimethylpyridine. That is, steric effects exerted by methyl groups in positions 3 and 5 are stronger than when they are in positions 2 and 6. Similarly, from the application of the DISQUAC (dispersive–quasichemical) model, it is possible to conclude that homocoordination is higher in systems with 3- or 4-methylpyridine than in those involving 2-methylpyridine.

Systems including aromatic hydrocarbons are nearly ideal, which seems to indicate that there is no specific interaction in such solutions. Mixtures with 1-alkanols show heterocoordination. This reveals the existence of interactions between unlike molecules, characteristic of alkanol + amine mixtures. Methanol systems show the lowest $S_{CC}(0)$ values due, partially, to size effects. This explains the observed decrease of homocoordination in such solutions in the order: pyridine > 2-methylpyridine > 2,6-dimethylpyridine. Moreover, as the energies of the OH–N hydrogen bonds are practically independent of the pyridine base considered when mixed with methanol, it suggests that size effects are predominant over steric hindrances to the creation of the OH–N hydrogen bonds, which are expected to increase with the number of methyl groups in the aromatic amine. For a given 1-alkanol (≠ methanol), $S_{CC}(0)$ varies in the sequence: pyridine > methyl pyridine ≈ 2,6-dimethylpyridine. For alkyl pyridines, stability seems to be independent of position and number of alkyl groups attached to the aromatic ring of the amine. Mixtures with isomeric 2-alkanols show lower heterocoordination, as the hydroxyl group is more sterically hindered than in 1-alkanols.

1. Introduction

In order to gain insight into the liquid state, thermodynamic properties such as molar excess enthalpy, H^E, molar excess volume, V^E, or molar excess isobaric heat capacity, C_P^E, of liquid mixtures can be examined taking into account the differences in molecular size and shape, anisotropy, dispersion and so forth. From this point of view, amines are a very interesting class of compounds. Primary and secondary amines are weakly self-associated [1–7]. 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 [8] (92.05 J mol^{-1} K^{-1}; for 1-alkanols [8], this constant is 110.88 J mol^{-1} K^{-1}). Nevertheless, the values of their effective dipole moments [9,10], $\bar{\mu}$, an useful magnitude to evaluate the impact of polarity on bulk properties, and of ΔT_b, the difference between the boiling temperatures of a given pyridine base and of its homomorphic hydrocarbon (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

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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 [88]; μ, dipole moment; $\bar{\mu}$, effective dipole moment.

[b] [88].

[c] [89].

[d] [62].

[e] [78].

[f] [90].

proposed [11–15]. 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 [12,13]. Alternatively, 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 [14,15]. The existence of pyridine dimers, which seems to be supported by X-ray and neutron diffraction [16] and by statistical mechanical simulation [17], has also been 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 the first step for a better understanding of the pyrrole ring, specially important to model typical binding sites on proteins [7].

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 [18,19]. There are at least two ways of looking at the fluctuations in a binary mixture [18–20]. 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 [21–23]. The second approach was developed by Bhatia and Thornton [24] and used in the study of liquid binary alloys [25,26] on the basis of the so-called Bhatia–Thornton partial structure factors. This approach was generalized [27–29] 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 [27–31]. More recently, Cobos [19] has discussed the correlation between the concentration–concentration structure factor with C_V^E (molar excess heat capacity at constant volume) and C_P^E.

Different theories 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 (extended real association solution) model [32,33] and aqueous solutions using the Kirkwood–Buff theory [34]. Unfortunately, ERAS does not represent the symmetry of the H^E curves of mixtures involving alkanes. The UNIQUAC (universal quasichemical) equation was modified to predict accurately vapor–liquid equilibria, VLE, data over a wide range of temperature [35]. In the framework of UNIFAC (universal functional activity coefficient) (Dortmund version [36]) interaction parameters for contacts between the pyridine group and other different groups are available [37]. In a recent work [38], we have studied pyridine systems in terms of DISQUAC (dispersive–quasichemical) [39], a purely physical model based on the rigid lattice theory developed by Guggenheim [40]. We have shown that the model describes rather accurately a whole set of thermodynamic properties such as VLE, G^E (molar excess Gibbs energies), LLE (liquid–liquid equilibria), SLE (solid–liquid equilibria), 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 [41].

This article is concerned with the investigation of mixtures containing pyridine or its alkyl derivatives in terms of the concentration–concentration structure factor, $S_{CC}(0)$. In addition, we also present, when possible, a detailed comparison between DISQUAC calculations and experimental $S_{CC}(0)$ values. The application of group contribution models to evaluate the G^E derivatives with the mole fraction is a useful technique in the absence of the needed experimental data. For example, UNIFAC has been used in the calculations of the Kirkwood–Buff integrals for some alkylbenzoate systems [42,43]. Nevertheless, it seems to be convenient to show firstly if the selected group contribution model describes accurately the available experimental data for the investigated mixtures.

2. Theory

2.1. The concentration–concentration structure factor

Mixture structure can be studied using the $S_{CC}(0)$ function [19,20,25,28], defined as [19,20,28,44]:

$$S_{CC}(0) = \frac{RT}{(\partial^2 G^M / \partial x_1^2)_{P,T}} = \frac{x_1 x_2}{D} \tag{1}$$

with

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

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

System	N^a	T/K	k^b	G^E/J mol^{-1}	$\sigma_r(P)^c$	Ref.
Pyridine + n-C$_6$	10	298.15	3	1080	0.017	[91]
	10	328.15	3	1030	0.015	[91]
Pyridine + n-C$_7$	9	298.15	3	1060	0.006	[91]
	16	313.15	3	1030	0.010	[92]
	9	333.15	3	988	0.004	[91]
	10	340.95	3	968	0.003	[93]
	12	353.15	2	910	0.001	[93]
Pyridine + n-C$_8$	12	313.15	3	1020	0.003	[92]
	14	353.15	2	889	0.003	[93]
	11	369.75	2	824	0.003	[93]
Pyridine + n-C$_9$	16	313.15	3	1010	0.003	[92]
	15	353.15	3	846	0.002	[93]
	12	369.75	2	839	0.005	[93]
Pyridine + n-C$_{10}$	10	353.15	3	984	0.003	[93]
	9	373.15	3	706	0.015	[93]
Pyridine + C$_6$H$_{12}$	12	293.15	3	934	0.005	[94]
	12	298.15	3	927	0.006	[94]
	12	313.15	2	896	0.005	[94]
2-Methylpyridine + n-C$_7$	16	313.15	3	771	0.002	[92]
2-Methylpyridine + n-C$_8$	16	313.15	2	771	0.003	[92]
2-Methylpyridine + n-C$_9$	15	313.15	3	750	0.004	[92]
3,5-Dimethylpyridine + n-C$_7$	7	273.15	3	827	0.007	[78]
	7	298.15	3	819	0.008	[78]
	7	343.15	3	725	0.008	[78]
3,5-Dimethylpyridine + n-C$_8$	7	273.15	3	870	0.010	[78]
	7	298.15	3	939	0.013	[78]
	7	343.15	3	763	0.011	[78]
2,6-Dimethylpyridine + n-C$_7$	9	263.15	3	645	0.004	[78]
	9	298.15	3	565	0.004	[78]
	9	343.15	3	473	0.006	[78]
2,6-Dimethylpyridine + n-C$_8$	8	263.15	3	654	0.005	[78]
	8	298.15	3	584	0.002	[78]
	8	343.15	3	481	0.003	[78]
Pyridine + C$_6$H$_6$	8	298.15	2	125	0.001	[95]
	8	323.15	2	132	0.005	[95]
2-Methylpyridine + C$_6$H$_6$	14	313.15	2	54	0.003	[92]
3-Methylpyridine + C$_6$H$_6$	16	313.15	3	65	0.002	[92]
4-Methylpyridine + C$_6$H$_6$	15	313.15	2	77	0.003	[92]
Pyridine + C$_7$H$_8$	10	298.15	3	225	0.007	[95]
	10	333.15	2	223	0.001	[95]
	12	373.15	1	213	0.0008	[96]
2-Methylpyridine + C$_7$H$_8$	16	313.15	2	114	0.003	[92]
	12	373.15	2	101	0.0002	[97]
3-Methylpyridine + C$_7$H$_8$	16	313.15	2	136	0.003	[92]
	11	373.15	2	148	0.0008	[98]
4-Methylpyridine + C$_7$H$_8$	16	313.15	3	152	0.001	[92]
2,4-Dimethylpyridine + 1,2-dimethylbenzene	12	373.15	1	88	0.001	[97]
2,6-Dimethylbenzene + 1,2-dimethylbenzene	12	373.15	1	63	0.0006	[97]
2,6-Dimethylbenzene + 1,3-dimethylbenzene	12	373.15	1	70	0.0004	[97]
2,6-Dimethylbenzene + 1,4-dimethylbenzene	11	373.15	1	75	0.0003	[97]
2,4,6-Trimethylpyridine + 1,3,5-trimethylbenzene	12	373.15	1	59	0.001	[99]
2,4,6-Trimethylpyridine + 2,4,6-trimethylbenzene	12	373.15	1	56	0.0006	[99]
Methanol + pyridine	10	298.15	3	−97	0.004	[85]
	10	308.15	3	−78	0.003	[85]
	17	313.15	3	−74	0.001	[100]
	10	318.15	3	−61	0.001	[85]
Ethanol + pyridine	15	313.15	2	−1.5	0.0004	[100]
	22	338.15	2	29	0.002	[86]
	23	348.15	2	36	0.005	[86]
1-Propanol + pyridine	15	313.15	2	−115	0.004	[100]
	23	343.15	2	−107	0.0009	[86]
	28	363.15	2	−115	0.007	[86]
1-Butanol + pyridine	14	313.15	2	−135	0.004	[100]
	24	343.15	2	−78	0.001	[86]

Table 2 (*Continued*)

System	N^a	T/K	k^b	G^E/J mol^{-1}	$\sigma_r(P)^c$	Ref.
	24	363.15	2	−108	0.001	[86]
Methanol + 2-methylpyridine	10	298.15	3	−249	0.002	[85]
	17	313.15	3	−193	0.005	[100]
	10	318.15	3	−171	0.001	[85]
Ethanol + 2-methylpyridine	14	313.15	2	−100	0.002	[100]
1-Propanol + 2-methylpyridine	14	313.15	2	−234	0.0006	[100]
1-Butanol + 2-methylpyridine	16	313.15	2	−274	0.002	[100]
Methanol + 3-methylpyridine	13	313.15	3	−129	0.010	[101]
Ethanol + 3-methylpyridine	13	313.15	2	−57	0.002	[101]
1-Propanol + 3-methylpyridine	15	313.15	2	−176	0.004	[101]
1-Butanol + 3-methylpyridine	13	313.15	2	−221	0.002	[101]
Methanol + 4-methylpyridine	14	313.15	3	−201	0.004	[101]
Ethanol + 4-methylpyridine	15	313.15	2	−112	0.002	[101]
1-Propanol + 4-methylpyridine	17	313.15	2	−234	0.002	[101]
1-Butanol + 4-methylpyridine	16	313.15	2	−266	0.003	[101]
Methanol + 2,6-dimethylpyridine	10	298.15	3	−285	0.008	[85]
	16	313.15	4	−219	0.004	[101]
	10	318.15	3	−188	0.006	[85]
Ethanol + 2,6-dimethylpyridine	12	313.15	3	−61	0.003	[101]
1-Propanol + 2,6-dimethylpyridine	16	313.15	2	−201	0.002	[101]
1-Butanol + 2,6-dimethylpyridine	15	313.15	2	−273	0.002	[101]
2-Propanol + pyridine	12	313.15	2	21	0.001	[102]
2-Butanol + pyridine	14	313.15	3	−119	0.0007	[102]
2-Propanol + 2,6-dimethylpyridine	14	313.15	2	71	0.001	[102]

[a] Number of experimental data points.

[b] Number of coefficients for G^E represented by a Redlich–Kister expansion.

[c] $\sigma_r(P) = \{(1/N) \sum [(P_{exp} - P_{calc})/P_{exp}]^2\}^{1/2}$.

D is a function closely related to thermodynamic stability [27,45,46]. For ideal mixtures, $G^{E,id} = 0$; $D^{id} = 1$ and $S_{CC}(0) = x_1 x_2$. As stability conditions require, $S_{CC}(0) > 0$, and if the system is close to phase separation, $S_{CC}(0)$ must be large and positive (∞, when the mixture presents a miscibility gap). In contrast, if compound formation between components appears, $S_{CC}(0)$ must be very low (0, in the limit). So, if $S_{CC}(0) > x_1 x_2$, 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 $0 < S_{CC}(0) < x_1 x_2 = S_{CC}(0)^{id}$, 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. So, $S_{CC}(0)$ is an useful magnitude to evaluate the non-randomness in the mixture [20,44].

2.2. The DISQUAC model

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 [47]. As volume and surface units, the volume R_{CH_4} and surface Q_{CH_4} of methane are taken arbitrarily [48]. Most of the geometrical parameters for the groups referred in this work are given elsewhere [38]. For the C_5H_3 group, $r_{C_5H_3} = 2.05944$ and $q_{C_5H_3} = 1.25814$, and for the C_5H_2 group, $r_{C_5H_2} = 1.91216$ and $q_{C_5H_2} = 1.02371$, (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 [48,49] must be considered. Thus,

$$G^E = G^{E,COMB} + G^{E,DIS} + G^{E,QUAC} \tag{3}$$

$$H^E = H^{E,DIS} + H^{E,QUAC} \tag{4}$$

(iii) the interaction parameters are assumed to be dependent on the molecular structure and (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^E and H^E in the framework of DISQUAC are given elsewhere [50]. The temperature dependence of the interaction parameters is expressed in terms of the DIS and QUAC interchange coefficients [50], $C_{st,l}^{DIS}$; $C_{st,l}^{QUAC}$ where $s \neq t$ are two contact surfaces present in the mixture and $l = 1$ (Gibbs energy), $l = 2$ (enthalpy), $l = 3$ (heat capacity).

In terms of the DISQUAC model:

$$\frac{D}{x_1 x_2} = \frac{1}{S_{CC}(0)} = \frac{1}{x_1 x_2} + \frac{1}{RT}\left(\frac{\partial^2 G^{E,COMB}}{\partial x_1^2}\right)_{P,T} + \frac{1}{RT}\left(\frac{\partial^2 G^{E,INT}}{\partial x_1^2}\right)_{P,T} \tag{5}$$

where $G^{E,INT} = G^{E,DIS} + G^{E,QUAC}$. Expressions for $(\partial^2 G^{E,COMB}/\partial x_1^2)_{P,T}$ and $(\partial^2 G^{E,INT}/\partial x_1^2)_{P,T}$ have been given elsewhere [51]. The combinatorial part only depends on r_i values and mole fractions [51]; it is always positive and hence causes heterocoordination.

3. Results and discussion

The G^E values obtained from VLE measurements and used for $S_{CC}(0)$ calculations are listed in Table 2. Results on $S_{CC}(0)$ for the studied mixtures are collected in Tables 3–5, which also show DISQUAC calculations, including the combinatorial and interactional contributions to $S_{CC}^{-1}(0)$. Results in a graphical way are shown, for some selected mixtures, in Figs. 1–5. In the following, we are referring to values of the thermodynamic properties at equimolar composition and 298.15 K

Table 3
Concentration–concentration structure factor, $S_{CC}(0)$, at temperature T and equimolar composition, for pyridine base (1) + alkane (2) mixtures.

System	T/K	$S_{CC}(0)$		$S_{CC}(0)^{-1}$		Ref.
		Exp.	DQ	Comb	Int.	
Pyridine + n-C$_6$	298.15	1.272	1.258	0.175	−3.380	[91]
	328.15	0.823	0.831		−2.972	[91]
Pyridine + n-C$_7$	298.15	1.093	1.220	0.302	−3.482	[91]
	313.15	1.013	0.956		−3.256	[92]
	333.15	0.705	0.758		−2.983	[91]
	340.95	0.662	0.706		−2.886	[93]
	353.15	0.658	0.642		−2.744	[93]
Pyridine + n-C$_8$	313.15	1.066	0.845	0.437	−3.253	[92]
	353.15	0.634	0.580		−2.713	[93]
	369.75	0.539	0.525		−2.532	[93]
Pyridine + n-C$_9$	313.15	0.920	0.772	0.572	−3.277	[92]
	353.15	0.634	0.539		−2.717	[93]
	369.75	0.551	0.489		−2.527	[93]
Pyridine + n-C$_{10}$	313.15		0.708	0.704	−3.291	
	353.15	0.518	0.501		−2.708	[93]
	373.15	0.459	0.449		−2.477	[93]
Pyridine + n-C$_{12}$	313.15		0.587	0.952	−3.248	
Pyridine + n-C$_{14}$	298.15		0.599	1.173	−3.503	
	313.15		0.511		−3.216	
Pyridine + n-C$_{16}$	298.15		0.548	1.369	−3.544	
	313.15		0.471		−3.246	
Pyridine + C$_6$H$_{12}$	293.15	0.875	0.850	0.089	−2.912	[94]
	298.15	0.841	0.806		−2.848	[94]
	313.15	0.801	0.699		−2.658	[94]
2-Methylpyridine + n-C$_6$	313.15		0.567	0.040	−2.276	
2-Methylpyridine + n-C$_7$	313.15	0.581	0.576	0.114	−2.378	[92]
2-Methylpyridine + n-C$_8$	313.15	0.613	0.577	0.208	−2.475	[92]
2-Methylpyridine + n-C$_9$	313.15	0.538	0.568	0.311	−2.550	[92]
2-Methylpyridine + n-C$_{10}$	313.15		0.556	0.419	−2.620	
2-Methylpyridine + n-C$_{12}$	313.15		0.523	0.634	−2.722	
2-Methylpyridine + n-C$_{16}$	313.15		0.458	1.028	−2.844	
3-Methylpyridine + n-C$_6$	313.15		0.779	0.040	−2.756	
3-Methylpyridine + n-C$_7$	313.15		0.755	0.114	−2.789	
3,5-Dimethylpyridine + n-C$_7$	273.15	1.00		0.025		[78]
	298.15	0.854				[78]
	343.15	0.616				[78]
3,5-Dimethylpyridine + n-C$_8$	273.15	0.753		0.078		[78]
	298.15	0.600				[78]
	343.15	0.428				[78]
2,6-Dimethylpyridine + n-C$_7$	263.15	0.558		0.025		[78]
	298.15	0.459				[78]
	343.15	0.402				[78]
2,6-Dimethylpyridine + n-C$_8$	263.15	0.516		0.078		[78]
	298.15	0.405				[78]
	343.15	0.340				[78]

3.1. Pyridine base + alkane mixtures

These systems are characterized by $S_{CC}(0) > 0.25$ (Table 3, Figs. 1–3), i.e., by interactions between like molecules (homocoordination). In agreement with this fact, they show usually positive H^E and V^E values [41,52–62] (see below), which increase with the chain length of the alkane. Therefore, the main contribution to these excess functions comes from the disruption of the amine–amine interactions. Structural effects are present in solutions with the shorter alkanes, as the S-shaped V^E curves reveal [59–62].

Homocoordination is rather strong for pyridine + alkane mixtures at 298.15 K, as they are fairly close to their corresponding upper critical solution temperatures (UCSTs) (e.g., 268.7 K for the system with dodecane [63]). DISQUAC represents fairly well the $S_{CC}(0)$ values (Table 3; Figs. 1–3). The poorer predictions are

encountered for the pyridine mixtures when the system temperature is not far from the UCST. It is known that antipathy between the system components is stronger at temperatures close to the UCST, where the divergence of the correlation length leads to the divergence of the concentration–concentration structure factor [20,28,64,65]. As a matter of fact, when an UCST is approached from the homogeneous region at constant pressure and at constant critical composition, $S_{CC}(0)$ tends to infinity [19] as $((T - T_c)/T_c)^{-\gamma}$ where, in the framework of the critical exponents theory, $\gamma = 1.240$, while for a mean field theory, as DISQUAC, $\gamma = 1$ [19,45]. In addition, one should keep in mind that critical effects on the thermodynamic properties of fluids are observed in practice over a large range of temperature and densities around the critical point [66]. Nevertheless, DISQUAC correctly describes the $S_{CC}(0)$ decrease when T is increased, in such way that a better representation is reached at higher temperatures (far from the UCST). This is supported by

Table 4
Concentration–concentration structure factor, $S_{CC}(0)$, at temperature T and equimolar composition, for pyridine base (1) + aromatic compound (2) mixtures.

System	T/K	$S_{CC}(0)$		$S_{CC}(0)^{-1}$		Ref.
		Exp.	DQ	Comb	Int.	
Pyridine + C_6H_6	298.15	0.278	0.278	0.006	−0.409	[95]
	323.15	0.2770	0.277		−0.396	[95]
2-Methylpyridine + C_6H_6	313.15	0.261	0.262	0.020	−0.203	[92]
3-Methylpyridine + C_6H_6	313.15	0.257	0.264	0.020	−0.232	[92]
4-Methylpyridine + C_6H_6	313.15	0.266	0.264	0.020	−0.232	[92]
Pyridine + C_7H_8	298.15	0.271	0.303	0.082	−0.782	[95]
	333.15	0.298	0.296		−0.704	[95]
	373.15	0.290	0.290		−0.633	[96]
2-Methylpyridine + C_7H_8	313.15	0.274	0.271	0.004	−0.314	[92]
	373.15	0.267	0.267		−0.259	[97]
3-Methylpyridine + C_7H_8	313.15	0.279	0.282	0.004	−0.458	[92]
	373.15	0.276	0.278		−0.407	[98]
4-Methylpyridine + C_7H_8	313.15	0.275	0.282	0.004	−0.458	[92]
2,4-Dimethylpyridine + 1,2-dimethylbenzene	373.15	0.265		0.003		[97]
2,6-Dimethylbenzene + 1,2-dimethylbenzene	373.15	0.260		0.003		[97]
2,6-Dimethylbenzene + 1,3-dimethylbenzene	373.15	0.262		0.003		[97]
2,6-Dimethylbenzene + 1,4-dimethylbenzene	373.15	0.263		0.003		[97]
2,4,6-Trimethylpyridine + 1,3,5-trimethylbenzene	373.15	0.260		0.002		[99]
2,4,6-Trimethylpyridine + 2,4,6-trimethylbenzene	373.15	0.260		0.002		[99]

Table 5
Concentration–concentration structure factor, $S_{CC}(0)$, at temperature T and equimolar composition, for pyridine base (1) + organic solvent (2).

| System	T/K	$S_{CC}(0)$		$S_{CC}(0)^{-1}$		Ref.
		Exp.	DQ	Comb	Int.	
Methanol + pyridine	298.15	0.224	0.235	0.477	−0.222	[85]
	308.15	0.229	0.239		−0.293	[85]
	313.15	0.233	0.241		−0.328	[100]
	318.15	0.233	0.242		−0.345	[85]
Ethanol + pyridine	313.15	0.250	0.251	0.109	−0.125	[100]
	338.15	0.255	0.251		−0.125	[86]
	348.15	0.256	0.250		−0.109	[86]
1-Propanol + pyridine	313.15	0.230	0.230	0.003	0.345	[100]
	343.15	0.232	0.230		0.345	[86]
	363.15	0.232	0.229		0.364	[86]
1-Butanol + pyridine	313.15	0.226	0.230	0.026	0.345	[100]
	343.15	0.237	0.227		0.379	[86]
	363.15	0.233	0.225		0.418	[86]
Methanol + 2-methylpyridine	298.15	0.200	0.220	0.773	−0.227	[85]
	313.15	0.210	0.228		−0.387	[100]
	318.15	0.212	0.231		−0.444	[85]
Ethanol + 2-methylpyridine	313.15	0.232	0.236	0.295	−0.058	[100]
1-Propanol + 2-methylpyridine	313.15	0.212	0.214	0.077	0.596	[100]
1-Butanol + 2-methylpyridine	313.15	0.206	0.209	0.004	0.781	[100]
Methanol + 3-methylpyridine	313.15	0.217	0.234	0.773	−0.499	[101]
Ethanol + 3-methylpyridine	313.15	0.239	0.237	0.295	−0.076	[101]
1-Propanol + 3-methylpyridine	313.15	0.220	0.215	0.077	0.574	[101]
1-Butanol + 3-methylpyridine	313.15	0.214	0.211	0.004	0.735	[101]
Methanol + 4-methylpyridine	313.15	0.210	0.234	0.773	−0.499	[101]
Ethanol + 4-methylpyridine	313.15	0.230	0.237	0.295	−0.076	[101]
1-Propanol + 4-methylpyridine	313.15	0.212	0.215	0.077	0.574	[101]
1-Butanol + 4-methylpyridine	313.15	0.207	0.211	0.004	0.735	[101]
Methanol + 2,6-dimethylpyridine	298.15	0.189		1.041		[85]
	313.15	0.203				[101]
	318.15	0.203				[85]
Ethanol + 2,6-dimethylpyridine	313.15	0.239		0.500		[101]
1-Propanol + 2,6-dimethylpyridine	313.15	0.217		0.206		[101]
1-Butanol + 2,6-dimethylpyridine	313.15	0.207		0.060		[101]
2-Propanol + pyridine	313.15	0.254		0.003		[102]
2-Butanol + pyridine	313.15	0.236		0.026		[102]
2-Propanol + 2,6-dimethylpyridine	313.15	0.264		0.206		[102]
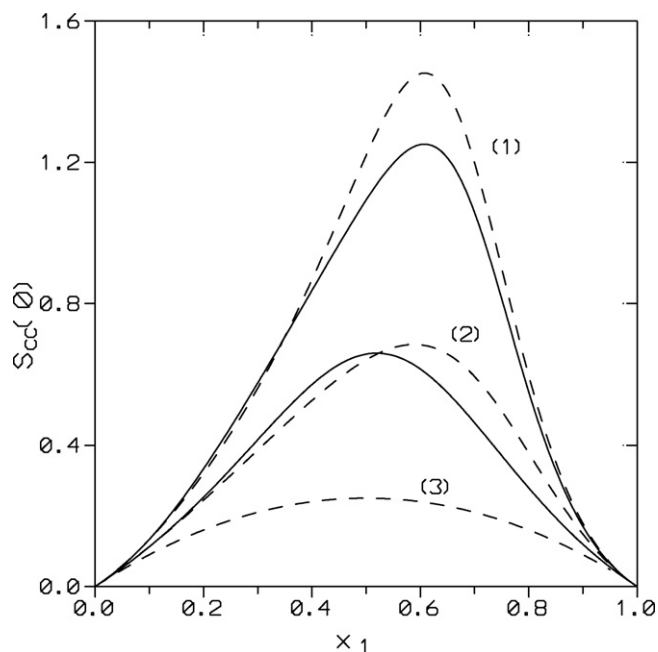
Fig. 1. $S_{CC}(0)$ for the pyridine (1) + heptane (2) mixture at temperature T: curve (1), $T = 298.15$ K; curve (2), $T = 353.15$ K. Solid lines, experimental values [91,93]; dashed lines, DISQUAC calculations; curve (3), ideal mixture.
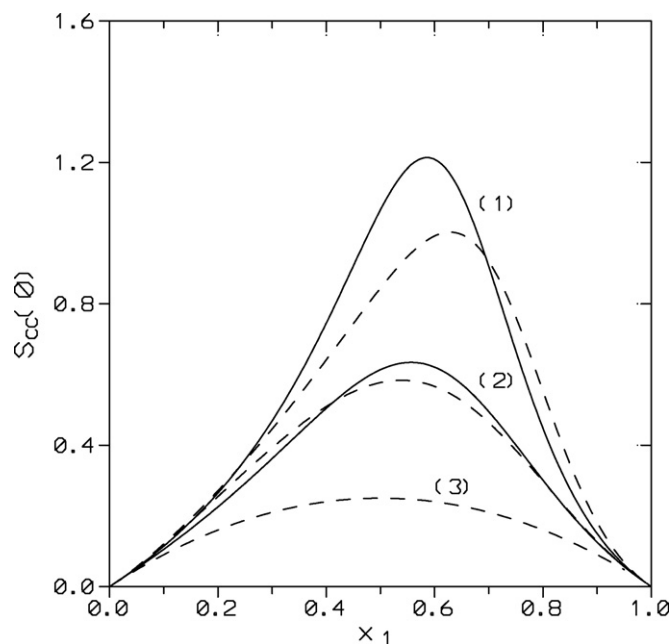

Fig. 3. $S_{CC}(0)$ for pyridine base (1) + octane (2) systems at 313.15 K: curve (1), pyridine mixture; curve (2), 2-methylpyridine system. Solid lines, experimental values [92]; dashed lines, DISQUAC calculations; curve (3), ideal mixture.

the results for, e.g., pyridine + decane or 2-methylpyridine + alkane systems (Table 3).

On the other hand, for pyridine mixtures, DISQUAC predicts $S_{CC}(0)(x_1)$ curves which are progressively shifted to the region rich in the amine when the alkane size increases. It should be remarked that, typically, for polar compound (dimethyl carbonate [67], acetic anhydride [68], 2-methoxyethanol [69–71], 2-ethoxyethanol [70]) + alkane systems, the corresponding LLE curves become skewed towards high mole fractions of the smaller component when both compounds differ considerably in size. In the case of pyridine solutions, this effect is probably overestimated

by the model due to: (i) the DISQUAC interaction parameters for the N/aliphatic contacts were adjusted in order to provide simultaneously a reasonable representation of the available VLE and LLE data for this type of mixtures [38], (ii) DISQUAC 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 critical functions [45]. For this reason, close to the critical point, it is not possible to describe simultaneously VLE and LLE data using the same set of interaction parameters [72].
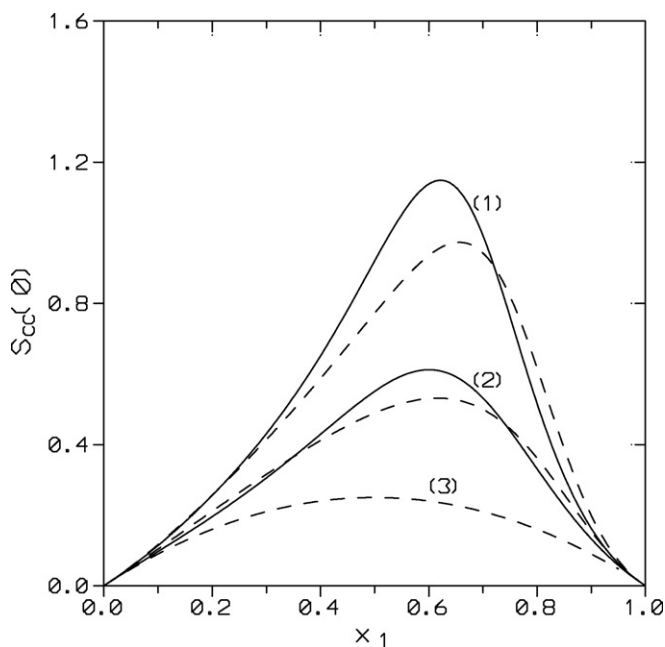

Fig. 2. $S_{CC}(0)$ for the pyridine (1) + nonane (2) mixture at temperature T: curve (1), $T = 313.15$ K; curve (2), $T = 369.75$ K. Solid lines, experimental values [92,93]; dashed lines, DISQUAC calculations; curve (3), ideal mixture.
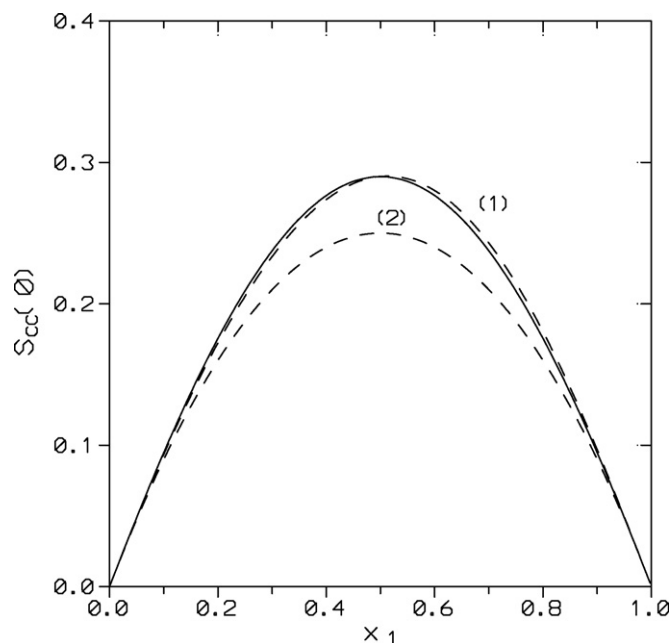

Fig. 4. $S_{CC}(0)$ for the pyridine (1) + toluene (2) mixture at 373.15 K: curve (1), solid line, experimental values [96]; dashed line, DISQUAC calculations; curve (2), ideal mixture.
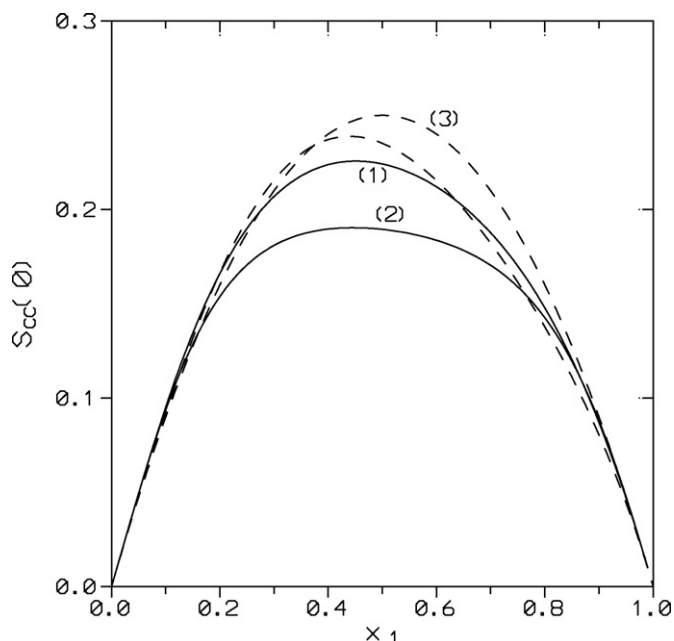
Fig. 5. $S_{CC}(0)$ for methanol (1) + pyridine base (2) systems at 298.15 K: curve (1), pyridine mixture; curve (2), 2,6-dimethylpyridine system. Solid lines, experimental values [85]; dashed line, DISQUAC calculations; curve (3), ideal mixture.

It is noteworthy that while both H^E and V^E functions increase with the chain length of the alkane in mixtures with a given pyridine base [41,52–62], $S_{CC}(0)$ decreases for the longer alkanes. This can be ascribed to size effects, as Table 3 reveals that the combinatorial contribution to $S_{CC}^{-1}(0)$ increases with the chain length of the alkane. A similar behaviour has been observed for benzene + alkane mixtures when they have been investigated in terms of the Flory–Huggins theory [20]. As a general rule, far from phase separation, differences in size prevent concentration fluctuations [23,73,74].

Size effects can be also examined comparing H^E and excess internal energy at constant volume, U_V^E (Table 6). Neglecting terms of higher order in V^E, U_V^E is displayed to a good approximation to [45,75]:

$$U_V^E = H^E - \frac{\alpha}{\kappa_T} T V^E \quad (6)$$

where α and κ_T are the isobaric thermal expansion coefficient and the isothermal compressibility factor of the mixture, respectively. Due to the lack of experimental data, these quantities were calculated as [76,77]:

$$M = \phi_1 M_1 + \phi_2 M_2 \quad (7)$$

In this expression, M is the value of α or κ_T for the mixture; M_i, the value of these magnitudes for the pure compound i (=1.2) (see Appendix A, Table A.1) and $\phi_i = x_i V_i/(x_1 V_1 + x_2 V_2)$. We newly note that the difference between U_V^E and H^E values increases with the chain length of the alkane.

For a given alkane, e.g., heptane, H^E decreases as follows: H^E(pyridine) = 1735 [52] > H^E(3-methylpyridine) = 1371 [54] > H^E (3,5-dimethylpyridine, T = 303.15 K) = 1236 [78] and H^E(pyridine) = 1735 [52] > H^E(2-methylpyridine) = 1346 [53] > H^E(2,4-dimethyl-pyridine) = 1100 [55] > H^E(2,4,6-trimethylpyridine) = 944 [56] (all values in J mol^{-1}). This reveals that the amine–amine interactions become weaker 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 (Table 1). The mentioned weakening of the amine–amine interactions also explains the V^E variation: V^E(pyridine + heptane) = 0.2657 [41] > V^E(2-methylpyridine + hept-

ane) = 0.1977 [57] > V^E(2,4-dimethylpyridine + heptane) = 0.117 [61] (values in cm^3 mol^{-1}). The $S_{CC}(0)$ change for a fixed alkane is: pyridine > 3,5-dimethylpyridine and pyridine > 2-methylpyridine > 2,6-dimethylpyridine. This suggests that the number of amine–amine interactions available to be broken upon mixing also decreases in the same sequences, probably due to steric hindrances exerted by the CH$_3$– groups of the pyridine base increase with the number of these groups.

The next step is to analyse the influence of the relative position of the methyl groups of the aromatic amines studied in the thermodynamic properties of the related systems. In mixtures with heptane, H^E changes in the sequences: 1407 (4-methylpyridine) [54] > 1371 (3-methylpyridine) [54] > 1346 (2-methylpyridine) [53] and 1235 (3,5-dimethylpyridine, T = 303.15 K) [78] > 1047 (2,4-dimethylpyridine) [55] > 1000 (2,6-dimethylpyridine, T = 303.15 K) [78], in agreement with the relative variations of the $\bar{\mu}$ and ΔT_b (Table 1). However, V^E varies in opposite way: V^E(2,4-dimethylpyridine) [61] = 0.117 < V^E(2,6-dimethylpyridine) [59] = 0.1847 cm^3 mol^{-1}. The different values of the molar volumes of these dimethylpyridines (Table 1) suggest that such behaviour might be due to packing effects. On the other hand, homocoordination is higher in solutions with 3,5-dimethylpyridine than in those with 2,6-dimethylpyridine (Table 3), which seems to reveal 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. Similarly, from DISQUAC calculations, it is possible to conclude that homocoordination is higher in systems with 3- or 4-methylpyridine than in those involving 2-methylpyridine (see Table 3).

As it is known, the $S_{CC}(0)$ function has been proposed as a measure of the non-randomness in the mixture. Some attempts have been developed in order to state a correlation between the maximum of the $S_{CC}(0)$ vs x_1 curve and the magnitude of the so-called w-shape effect (a w-shaped composition dependence of the C_P^E). This effect is more intense when the difference in size between components is increased, as in the case of pyridine + alkane mixtures [41]. In addition, at equimolar composition and 298.15, $S_{CC}(0)$ = 0.7 K has been established as a threshold value for the appearance of w-shaped C_P^E curves for systems without specific interactions [20]. So, Rubio et al. [20] have shown that for a "w-shape" to appear a negative C_P^E background is necessary, and this seems not to be hold for systems with specific interactions such as acetonitrile + CCl$_4$, or + 1-butanol. However, here we found that for the pyridine + heptane mixture, $S_{CC}(0) > 0.7$ and the corresponding C_P^E curve is not w-shaped. It should be remarked that Cobos has shown that C_P^E (more properly C_V^E) and $S_{CC}(0)$ supply different information on the binary mixture. The $S_{CC}(0)$ function is related to the condition of thermodynamic stability, and C_V^E is related to the temperature variation of the effective pairwise interactions between molecules. Nevertheless, the maximum of the $S_{CC}(0)$ curves is progressively shifted to high mole fractions of pyridine when the chain length of alkane increases, i.e., to the region where the C_P^E curve shows the maximum.

3.2. Pyridine base + aromatic compound mixtures

Now the $S_{CC}(0)$ curves show a behaviour close to the ideal one ($S_{CC}(0) \approx 0.25$, Table 4, Fig. 4). This may be interpreted assuming that no specific interactions exist in the present systems. Several evidences support this conclusion: (i) the low H^E values of these solutions: H^E(pyridine + benzene) = 8 [79] or H^E(3,5-dimethylpyridine + benzene) = 33 J mol^{-1} [80]; (ii) the solid–liquid phase diagram of the pyridine + benzene mixture, characterized by a simple eutectic point [81]; (iii) the weak temperature dependence of the $S_{CC}(0)$ function (Table 4) and of H^E [80], which point out to the great stability of these systems. Finally, it should be remarked that

Table 6
Molar excess functions: enthalpies, volumes and internal energies at constant volume for pyridine base + organic solvent mixtures at equimolar composition and 298.15 K.

System	$H^E/\mathrm{J\,mol^{-1}}$	Ref.	$V^E/\mathrm{cm^3\,mol^{-1}}$	Ref.	$U_V^E/\mathrm{J\,mol^{-1}}$
Pyridine + n-C$_7$	1735	[52]	0.2657	[41]	1656
Pyridine + n-C$_{10}$	1963	[52]	0.689	[41]	1736
Pyridine + n-C$_{16}$	2351	[52]	1.116	[41]	1979
Methanol + pyridine	−711	[84]	−0.483	[85]	−540
Methanol + 2-methylpyridine	−1261	[84]	−0.958	[85]	−924
Methanol + 2,6-dimethylpyridine	−1626	[84]	−1.503	[85]	−1076

DISQUAC provides an accurate description of the thermodynamic properties of the pyridine + C$_6$H$_6$ mixtures, under the assumption that the aromatic/N contacts are represented by dispersive interaction parameters only [38].

3.3. Alkanol + pyridine base mixtures

Systems with shorter 1-alkanols (from methanol to 1-butanol) show heterocoordination, ($S_{CC}(0) < 0.25$, Table 5, Fig. 5), which may be partially ascribed to the existence of interactions between unlike molecules, characteristic of alkanol + amine mixtures [4,10,82,83]. As usually, H^E and V^E increase with the chain length of the alcohol [38]. So, for pyridine mixtures H^E(methanol) = −711 [84] > H^E(1-butanol) = 182 J mol^{-1} [33] and V^E(methanol) = −0.483 [85] > V^E(ethanol) = −0.372 [86] > V^E(1-propanol) > −0.287 [86] > V^E(1-butanol) = −0.187 cm^3 mol^{-1} [86]. In contrast, for a given pyridine base, both G^E and $S_{CC}(0)$ decrease from ethanol when the size of the 1-alkanol is increased. 1-Alkanol + fixed alkane mixtures behave similarly. Such trend merely underlines that while there is a certain correlation between $S_{CC}(0)$ and G^E, there is no correlation with the magnitude of any other excess function [20]. It is remarkable that methanol systems are characterized by the lowest $S_{CC}(0)$ values. This is due, at least in part, to size effects. Note the large contribution to $S_{CC}(0)^{-1}$ from the combinatorial term (Table 5) and the large difference between H^E and U_V^E for these systems (Table 6). For mixtures with longer 1-alkanols, e.g., 1-octanol, DISQUAC also predicts heterocoordination ($S_{CC}(0) = 0.234$), as size effects become newly important (combinatorial contribution to $S_{CC}(0)^{-1}$ is _ca._ 0.5). Here, it may be pertinent to remember that a similar behaviour is encountered for pyridine + longer alkanes (see above).

H^E and V^E of mixtures containing methanol decrease when the size of the aromatic amine increases in the same order than in systems with a given alkane. In the case of V^E [85]: −0.483 (pyridine) > −0.958 (2-methylpyridine) > −1.503 (2,6-dimethylpyridine) (values in cm^3 mol^{-1}), and for H^E [84]: −711 (pyridine) > −1261 (2-methylpyridine) > −1635 (values in J mol^{-1}). This variation can be explained by the lower positive contribution to H^E from the disruption of the amine–amine interactions when passing from pyridine to 2,6-dimethylpyridine, as $\bar{\mu}$ and ΔT_b also decreases in the same order (Table 1). Moreover, the 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 [84], i.e., the energies of the OH–N hydrogen bonds are practically independent of the pyridine base considered [84] ($\approx$−31 kJ mol^{-1}). $S_{CC}(0)$ also changes in the sequence pyridine > 2-methylpyridine > 2,6-dimethylpyridine (Table 5). This seems to indicate that size effects are predominant over steric hindrances to the creation of the OH–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 5, see also Table 6). For a given 1-alkanol ($\neq$ methanol), $S_{CC}(0)$ varies in the

sequence: pyridine > methyl pyridine $\approx$ 2,6-dimethylpyridine. For alkyl pyridines, stability seems to be independent of position and number of alkyl groups attached to the aromatic ring.

When replacing 1-alkanol for an isomeric 2-alkanol in systems with a fixed pyridine base, $S_{CC}(0)$ increases (Table 5). So, mixtures with 2-alkanols are characterized by a lower heterocoordination, as the creation of interactions between unlike molecules becomes more difficult due to the hydroxyl group is sterically hindered in secondary alcohols. The higher H^E values (593 J mol^{-1} for 2-butanol + pyridine [87]) compared with those of 1-alkanol mixtures are consistent with this behaviour.

4. Conclusions

Pyridine base + alkane, or +aromatic hydrocarbon, or +1-alkanol mixtures have been studied using the $S_{CC}(0)$ function. Systems containing alkanes are characterized by homocoordination. In pyridine + alkane mixtures, $S_{CC}(0)$ decreases with the chain length of the longer alkanes, due to size effects. For a given alkane, $S_{CC}(0)$ also decreases with the number of CH$_3$– groups in the pyridine base, probably due to steric hindrances exerted by the CH$_3$– groups of the pyridine base increase with the number of these groups. Moreover, steric effects exerted by methyl groups in positions 3 and 5 are stronger when they are in positions 2 and 6. Systems including aromatic hydrocarbons are nearly ideal, which seems to indicate that there is no specific interactions in such solutions. Mixtures with 1-alkanols show heterocoordination, which is attributed to the existence of interactions between unlike molecules. For methanol systems, heterocoordination increases in the sequence: pyridine < 2-methylpyridine < 2,6-dimethylpyridine, due to size effects. As the energies of the OH–N hydrogen bonds are practically independent of the pyridine base considered, it suggests that size effects are predominant over steric hindrances to the creation of the OH–N hydrogen bonds. For a given 1-alkanol ($\neq$ methanol), $S_{CC}(0)$ varies in the sequence: pyridine > methyl pyridine $\approx$ 2,6-dimethylpyridine. For alkyl pyridines, stability seems to be independent of position and number of alkyl groups attached to the aromatic ring of the amine. Mixtures with isomeric 2-alkanols show lower heterocoordination, as the hydroxyl group is more sterically hindered than in 1-alkanols.

Appendix A.

Table A.1.

Table A.1

Physical constants at 298.15 K of pure compounds: molar volumes, V (for pyridine bases, see Table 1) coefficients of thermal expansion, α, and isothermal compressibility, κ_T.

Compound	$V/cm^3\,mol^{-1}$	$\alpha/10^{-3}\,K$	$\kappa_T/10^{-12}\,Pa^{-1}$
Pyridine		1.070[a]	699.6[b]
2-Methylpyridine		0.989[a]	753.4[b]
3-Methylpyridine		0.969[a]	710[c]
4-Methylpyridine		0.965[a]	691.9[c]
2,4-Dimethylpyridine		0.841[a]	964[e]
2,6-Dimethylpyridine		0.982[a]	1053[f]
3,5-Dimethylpyridine		0.898[d]	964[e]
2,4,6-Trimethylpyridine		0.988[b]	1059[g]
Heptane	147.45[a]	1.256[h]	1460.6[a]
Decane	195.89[a]	1.051[h]	1109.6[h]
Hexadecane	294.09[i]	0.883[h]	862[h]
Methanol	40.75[a]	1.196[a]	1248[a]

[a] [88].

[b] [62].

[c] [103].

[d] [78].

[e] From adiabatic compressibilities measurements [104] using heat capacities from Ref. [105].

[f] From adiabatic compressibilities measurements [106] using heat capacities from Ref. [105].

[g] From adiabatic compressibilities measurements [107] using heat capacities from Ref. [105].

[h] [108].

[i] [109].

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