



Isothermal vapor–liquid equilibria and excess molar enthalpy of 2-methylpyrazine (2MP) containing binary mixtures. Comparison with DISQUAC predictions



Hamama Ben-Makhlouf-Hakem^{a,*}, Ahmed Ait-Kaci^a, Jacques Jose^b

^a Laboratoire de Thermodynamique des Modelisation moleculaire, Faculté de chimie, USTHB, BP, 32 El-Alia, 16111 Bab Ezzouar, Algeria

^b Laboratoire des Sciences Analytiques, UMR 5280, Université Claude Bernard (Lyon 1), 43 Boulevard du 11 novembre 1918, 69622 Villeurbanne Cedex, France

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ABSTRACT

The vapour pressures of binary mixtures 2-methylpyridine with cyclohexane, *n*-heptane or toluene were measured by a static method in the range from 263.15 to 353.15 K. The pure components vapour pressures data and those of the mixtures were correlated with the Antoine equation. The excess enthalpies were measured at 303.15 K, by means of an isothermal calorimeter (C80 SETARAM model). The molar excess Gibbs energies, calculated from the vapour–liquid equilibrium data and the molar excess enthalpies compared satisfactorily with group contribution model (DISQUAC).

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1. Introduction

In our previous papers, we have studied the thermodynamic properties of binary mixtures 2,6- or 3,5-dimethylpyridine with alkanes [1], toluene [2] and cyclohexane [3]. Results were successfully interpreted by using the quasi-lattice group contribution theory (DISQUAC) [4] confirming the presence of intermolecular effects in tertiary heterocyclic amines.

Pyrazines and its derivatives form an important class of compounds which are present in many natural flavors and complex organic molecules. Thus, the 2-methylpyrazine is used in food flavors and baccy. This molecule which is an intermediate for aldinamide and hydraqogue has several commercial applications, such as in the synthesis of antituberculosis drug [5,6].

Despite their structural and electronic similarity to benzene and pyridine, few experimental thermodynamic studies are reported in the open literature for pyrazines and derivatives. Experimental data on 2-methylpyrazine are scarce, they are limited to excess volume and the vapour–liquid equilibria at $T=353.15$ K, for binary or ternary systems [6–8].

From a theoretical point of view, pyrazines with two nitrogen atoms in their ring are particularly interesting molecules for testing group-contribution models.

The purpose of the present work is to investigate VLE and excess enthalpy H^E in binary mixtures containing 2-methylpyrazine + *n*-heptane, + cyclohexane and + toluene. The experimental data were described using the DISQUAC model [4].

2. Experimental

2.1. Materials

The chemicals used in this study were 2-methylpyrazine, toluene, *n*-heptane and cyclohexane. The suppliers, formulas and purities of the pure components are shown in Table 1. All liquids were used as received and thoroughly degassed before measurements. Gas chromatography (GC) analysis of the chemicals revealed no significant impurities.

2.2. Apparatus and procedure

The experimental H^E data were measured, at atmospheric pressure, by means of a microcalorimeter, C80 (SETARAM model, Lyon, France). The temperature T was maintained constant at 303.15 ± 0.02 K. The mercury is used to separate the two small chambers containing the liquids to be mixed, housed in the calorimetric cell. The performance of the apparatus was checked

* Corresponding author. Tel.: +213 771399348; fax.: +213 21247107.

E-mail addresses: hamamahakem@yahoo.fr, hamamahakem@gmail.com (H. Ben-Makhlouf-Hakem).

Table 1

Provenance and purity of the chemicals used in this study.

Component	Formula	CAS number	Source	Claimed purity (mass fraction)	GC peak area (area fraction)
Methylpyrazine	C ₅ H ₆ N ₂	[109-08-0]	Fluka	≥0.990	0.999
Toluene	C ₇ H ₈	[108-88-3]	Sigma-Aldrich	>0.993	0.999
<i>n</i> -Heptane	C ₇ H ₁₆	[142-82-5]	Fluka	>0.990	0.999
Cyclohexane	C ₆ H ₁₂	[110-82-7]	Acros	>0.997	1.000

by determining H^E of cyclohexane + benzene at $T = 298.15$ K, our results differ by less than 2% from those reported by Marsh [9]. The estimated uncertainties in the mole fraction x_i and H^E are $u(x_i) = 0.002$ and $u(H^E) = 5$ J mol⁻¹ respectively.

The total vapour pressure measurements were carried out following the static method described elsewhere by Blondel-Tellouk et al. [10], of which only the most salient points are given here. The setup allows measurements at pressures from $(-133$ to $200 \times 10^3)$ Pa using two pressure sensors: MKS gage (Model 615D, MKS instrument, USA) for the pressure range $(-133$ to $1333)$ Pa and a Rosemount gage (Model 1151 DPE 2252, Minneapolis, Minn., USA) for the pressure range $(-1333$ to $200 \times 10^3)$ Pa. The pressure measurement consisted of applying the vapour pressure of the sample on the measurement side of the gauge. The reference side being submitted to a permanent-dynamic pumping, the residual pressure was 10^{-4} Pa and therefore could be neglected. The gauge was checked periodically against a Hg manometer Bouty (Paris, France) 70298 type cathetometer.

Temperatures were measured with a copper-constantan thermocouple calibrated with a platinum resistance thermometer (± 0.001 K, IPTS 90) and a Leeds Northup bridge. The uncertainties of our measurements are estimated to be ± 0.02 °C in the investigated temperature range, 0.2% for mole fraction, 3% for pressure lower than 600 Pa, 1% in the pressure range $700 \leq p$ (Pa) ≤ 1300 and 0.3% for the pressure range $1300 \leq p$ (Pa) ≤ 200000 .

Mixture compositions were prepared by mass and degassed as described previously by Blondel-Tellouk et al. [10]. The final composition of the liquid was determined after each pressure measurement by gas-liquid chromatography (Delsi instrument, Di 200, used a capillary column (\emptyset (100/120 mesh Hays SPQ) and 2 m long with a FID detector).

Table 2Experimental excess enthalpy at $T = 303.15$ K.

X_1	H^E (J mol ⁻¹)	X_1	H^E (J mol ⁻¹)
2-Methylpyrazine (1) + toluene (2)			
0.156	28	0.475	75
0.256	48	0.561	69
0.421	73	0.698	39
0.465	75	0.760	29
2-Methylpyrazine (1) + cyclohexane (2)			
0.094	680	0.566	1505
0.153	977	0.639	1383
0.251	1287	0.766	1012
0.381	1489	0.845	732
0.474	1522		
2-Methylpyrazine (1) + <i>n</i> -heptane (2)			
0.082	563	0.523	1543
0.175	1077	0.622	1440
0.335	1475	0.704	1247
0.411	1543	0.809	965
0.481	1550	0.877	697

$u(T) = \pm 0.02$ K; $u(H^E) = 5$ J mol⁻¹; $u(x_1) = \pm 0.002$.

3. Results

Experimental molar excess enthalpies H^E at 303.15 K are endothermic. They are reported in Table 2. The results have been fitted to the Redlich-Kister type equation:

$$H^E = x_1(1 - x_1) \sum_{i=1}^n a_i (2x_1 - 1)^{i-1} \quad (1)$$

The values of the coefficients a_i and the standard deviations $\delta(H^E)$, given by:

$$\delta(H^E) = \left[\frac{\sum_{i=1}^n (H^E - H_{\text{exp}}^E)^2}{(N - n)} \right]^{1/2} \quad (2)$$

were determined by least-squares analysis and are reported in Table 3. N is the number of experimental points and n the number of coefficients a_i .

The pure components vapour pressures data used in the Barker's method given in Table 4. They have been correlated with the Antoine equation. The results are summarized in Table 5.

Vapour phase imperfection and variation of the Gibbs energy of the pure liquid components with pressure were accounted for in terms of the 2nd molar virial coefficients and the molar volumes under saturation pressure as follows.

$$P = \sum_{i=1}^2 x_i P_i^0 \exp \left[\frac{g_i^E - (B_{ii} - V_i^0)(P - P_i^0) - 2PB_{12}(1 - y_i)^2}{RT} \right] \quad (3)$$

$$y = \frac{x_i P_i^0}{P} \exp \left[g_i^E - (B_{ii} - V_i^0)(P - P_i^0) - 2PB_{12}(1 - y_i)^2 \right] \quad (4)$$

$$B^E = B_{12} - \frac{(B_{11} + B_{12})}{2}; P_i^0 = P_{(x_i=1)} \quad (5)$$

where V_i^0 is the molar volume of the pure compound estimated with the Rackett equation, using the literature data for the acentric factor and critical properties [11]. The 2nd molar virial coefficients B_{ii} were evaluated with the Tsonopoulos method [12,13]. The values are reported in Table 6. Vapour pressures measurements, at different temperatures, are given in Table 7 together with the activity coefficients γ_1 and γ_2 and the excess molar Gibbs energies G^E calculated by the Barker's method [14], on the assumption that:

$$\frac{G^E}{RT} = x_1(1 - x_1) \sum_{i=0}^{m-1} A_i (2x_1 - 1)^i \quad (6)$$

with the standard deviation

$$\delta = \left\{ \frac{1}{n - m} \sum_{i=0}^n \left[\frac{(P_{\text{exp}} - P_{\text{calc}})}{P_{\text{exp}}} \right]^2 \right\}^{1/2} \quad (7)$$

where x_1 is the molar fraction of 2- methylpyrazine, n , the number of experimental points and m the number of coefficients A_i .

The parameters A_i and the standard deviation δ for the pressure are given in Table 8. $(G^E/T)_{x_1=0.5}$ at the equimolar concentration 0.5 was fitted with a second degree polynomial in $1/T$, for the binary

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