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# Internal Pressure in Binary Mixtures of Methylpyridine Isomers with $H_2O$ and $D_2O$

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**Abstract** Internal pressures and their excesses were calculated in the strict thermodynamic way for binary mixtures of 2-,3-,4-methylpyridine, 2,6-dimethylpyridine, and 2,4,6-dimethylpyridine with water and heavy water at $T = 296.15$ K. The excess internal pressure approach proved to be useful in studies of relatively subtle thermodynamic effects. Positive correlation was found between the association energy of the 1:1 water–amine complexes and the maximum values of the excess internal pressure. It was shown that the differences caused by the exchange of $H_2O$ by $D_2O$ in the mixtures are evident in the excess internal pressure isotherms. The larger excesses for the $D_2O$ mixtures may indicate that the difference in energy between the O–D· · ·N and O–D· · ·O bonds is higher than that between the O–H· · ·N and O–H· · ·O ones. That probably leads to different phase properties of the studied systems.

**Keywords** Hydration · Hydrogen bond · *Ortho* effect · Thermodynamic excess

## 1 Introduction

Mixtures of methylpyridine isomers with water are convenient model systems for studies of association and solvation processes that play a crucial role in biochemistry. These processes are often discussed in terms of hydrophobic and hydrophilic phenomena. Methylpyridines belong to the class of mixed solvents—in the properties of aqueous solutions of methylpyridines, both hydrophobic as well as hydrophilic effects are revealed. Molecules of methylpyridines (Fig. 1) have two acceptors of protons: the

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This paper is dedicated to Prof. Dr. Stefan Ernst on the occasion of his 75th birthday.

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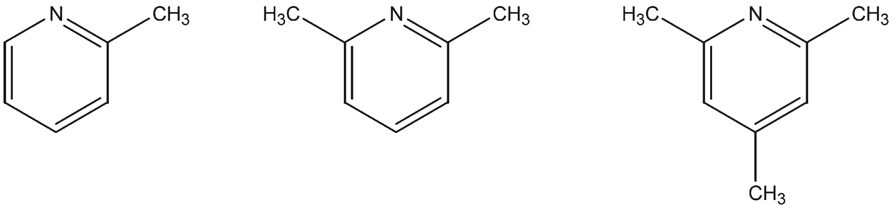

**Fig. 1** Structural formulas of 2-methylpyridine, 2,6-dimethylpyridine, and 2,4,6-trimethylpyridine

nitrogen atom and the $\pi$ electrons of the ring. The former is much stronger, and the hydrogen bonds between that atom and a hydrogen-donor molecule are readily formed. In aqueous solutions, the formation of O–H···N bonds is energetically favorable; their energy estimated by *ab initio* studies is $27.2\,\text{kJ}\cdot\text{mol}^{-1}$, while that of O–H···O bonds is $20.5\,\text{kJ}\cdot\text{mol}^{-1}$ [1]. Crystallographic experiments confirm the O–H···N hydrogen bonding in the solid trihydrates of pyridine [2] and 4-methylpyridine [3]. The O–H···N bond energy increases on substitution of the $CH_3$ groups in the positions 2 and 6 in the ring, i.e., in the vicinity of the nitrogen atom. That was confirmed by theoretical calculations [4] and the results of calorimetric studies [5,6].

The O–H···N bonds and the hydration shell around the non-polar part of the methypyridine molecules cause that the mixtures are thermodynamically non-ideal. As evidenced by the excess enthalpies, this non-ideality increases as $H_2O$ is replaced by $D_2O$ in the mixture [7]. However, the differences in excess enthalpies between the mixtures containing $H_2O$ and $D_2O$ are rather small. On the other hand, the replacement of $H_2O$ by $D_2O$ leads to spectacular phase effects, e.g., the development of the miscibility gap in the systems 2-methylpyridine–water and 3-methylpiridine–water [8].

This study was aimed at finding whether the changes in properties of the methylpyridines–water systems, caused by two reasons: the substitution of $CH_3$ groups in the pyridine ring and replacement of $H_2O$ by $D_2O$, are reflected in the internal pressure and its thermodynamic excess. The internal pressure is the partial derivative of the internal energy, $U$, with respect to the volume, $V$, at constant temperature, $T$:

$$p_{\text{int}} \equiv (\partial U/\partial V)_T. \tag{1}$$

Equation 1 can be transformed into the following formula:

$$p_{\text{int}} = TE/K_T - p, \tag{2}$$

where $p$ is the ambient pressure, $E$ is the isobaric expansion, $E \equiv (\partial V/\partial T)_p$, and $K_T$ is the isothermal compression, $K_T \equiv -(\partial V/\partial p)_T$. Thus, the internal pressure depends on the material constants: the isobaric thermal expansibility ($\alpha_p = E/V$) and the isothermal compressibility ($\kappa_T = K_T/V$).

In the last years, growing interest has been observed in the determination of the internal pressure. Apart from the studies of mixtures, the investigations of liquids at high pressures seem to be particularly interesting [9,10].

## 2 Calculations

Internal pressures and excess internal pressures were calculated for eight binary systems at 296.15 K and atmospheric pressure. Five mixtures contained $H_2O$ and 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 2,6-dimethylpyridine, or 2,4,6-trimethylpyridine, while the other three contained $D_2O$ and 2-methylpyridine, 3-methylpyridine, or 4-methylpyridine. In the calculations, Eq. 2 was used with $K_T$ given by the well-known relationship,

$$K_T = V\kappa_S + TE^2/C_p, \tag{3}$$

where $C_p$ is the isobaric heat capacity and $\kappa_S$ is the isentropic compressibility, and $\kappa_S \equiv -1/V(\partial V/\partial p)_S$. For the extensive functions $V$, $E$, and $C_p$ in Eqs. 2 and 3, their molar counterparts were substituted. The isentropic compressibilities were calculated from Laplace's formula,

$$\kappa_S = \rho^{-1}u^{-2}, \tag{4}$$

using the speeds of sound, $u$, and densities, $\rho$, reported in earlier studies [11–21]. Densities and thermal expansibilities of $H_2O$ and $D_2O$ were calculated from the equations of [22] and [23], respectively. Unfortunately, there are no heat capacities of the mixtures available in the literature. Thus, the ideal mixture approximation was applied;

$$C_p = \sum_{i=1}^{2} x_i C^{\circ}_{p,i}, \tag{5}$$

where $x_i$ is the mole fraction, $i = 1$ for amine and $i = 2$ for water, and superscript "o" denotes a pure substance. The heat capacities of the pure substances were taken from the following sources: $H_2O$ [24], $D_2O$ [25], 2-, 3- and 4-methylpyridine [26], 2,6-dimethylpyridine [27], and 2,4,6-trimethylpyridine [17]. Although rather rough, the last approximation is reasonable. That can be proved in the following way. Assuming that the excess heat capacity, i.e., the heat of mixing, is given by a parabolic function with a maximum at the mole fraction 0.5, where its value is arbitrarily set as 10 % of the heat capacity itself, and leaving the other data unchanged, one can calculate a new set of the hypothetical internal pressures. The latter differ from those reported here by ca. 2.5 % in the most unfavorable case. Thus, the internal pressure isotherms remain virtually unaffected. A similar difference for the excess internal pressures, calculated in the way reported below, reaches 5 % of the maximum excess value.

The excess internal pressure was calculated from the following formula [28]:

$$p^{\mathrm{E}}_{\mathrm{int}} = p_{\mathrm{int}} - \sum_{i=1}^{2} \psi_i p^{\circ}_{\mathrm{int},i}, \tag{6}$$

where $\psi_i$ is the compression fraction:

$$\psi_k = x_k K^{\circ}_{T,k} \Big/ \sum_{i=1}^{2} x_i K^{\circ}_{T,i}, \tag{7}$$

and $k = 1$ (amine) or $k = 2$ (water). In this approach, the thermodynamically ideal mixture is the reference state. It should be stressed that the excesses calculated from thermodynamically correct Eq. 6 differ from the deviations of $p_{\text{int}}$ from the mole-fraction-weighted average of the internal pressures of pure substances. The deviations, still sometimes reported in the literature as "excesses," have no physical meaning due to an incorrect reference state.

## 3 Results

Internal pressures and their excess values at $T = 296.15\,\text{K}$ are reported in Tables 1, 2 and 3. Figure 2 illustrates the influence of the number and positions of the $CH_3$ groups in the pyridine ring on the internal pressure. The internal pressure in pure amines increases in the following order: 2,4,6-tmpy $\approx$ 2,6-dmpy $<$ 2-mpy $<$ 4-mpy $\approx$ 3-mpy. In the same order, maxima of the $p_{\text{int}}$ isotherms decrease and shift slightly toward higher $x_1$ values. In spite of different internal pressures of $H_2O$ and $D_2O$, equal to $(1.55 \text{ and } 1.06) \times 10^8$ Pa, respectively, the internal pressure of mixtures seems to depend rather weakly on the isotopic composition of water. Differences between isotherms for the $H_2O$ and $D_2O$ systems are hardly noticeable, except those for 4-methylpyridinic mixtures at low mole fractions of the amine (Fig. 2a). The differences, however, are evident in the excess functions, as is illustrated in Fig. 3.

The excess internal-pressure isotherms were approximated by Redlich–Kister polynomials of the following form:

$$p^{\text{E}}_{\text{int}} \times 10^{-8}/\text{Pa} = \psi_1 \psi_2 \sum_{i=0}^{2} a_i (\psi_2 - \psi_1)^i, \tag{8}$$

where $a_i$'s are the regression coefficients, found by the least-squares method. Equation 8, with the $a_i$ coefficients the same as for the 2,6-dimethylpyridine–$H_2O$ system, describes the $p^{\text{E}}_{\text{int}}$ isotherm of the 2,4,6-trimethylpyridine-rich mixture. For dilute solutions of 2,4,6-trimethylpyridine, the following parabolic equation proved to be sufficient:

$$p^{\text{E}}_{\text{int}} \times 10^{-8}/\text{Pa} = a_1 \psi_1 + a_2 \psi_1^2, \tag{9}$$

where $a_i$'s are the regression coefficients, found by the least-squares method. The coefficients of Eqs. 8 and 9 are reported in Table 4.

## 4 Discussion and Conclusions

The internal pressure defined by Eq. 1 has a clear thermodynamic sense. That does not mean, however, that its discussion in terms of intermolecular interactions is

**Table 1** Internal pressures in binary mixtures of monomethylpyridines with $H_2O$ and their excess values at $T = 296.15$ K

| System | Mole fraction of (1) | Compression fraction of (1) | Internal pressure × $10^{-8}$ (Pa) | Excess internal pressure × $10^{-8}$ (Pa) | Data source |
|---|---|---|---|---|---|
| 2-mpy (**1**) + $H_2O$ (**2**) | 0 | 0 | 1.547 | | [11,22] |
| | 0.0201 | 0.1525 | 2.282 | 0.363 | [12] |
| | 0.0357 | 0.2454 | 2.835 | 0.689 | [12] |
| | 0.0450 | 0.2925 | 3.161 | 0.900 | [12] |
| | 0.0502 | 0.3170 | 3.238 | 0.917 | [12] |
| | 0.0552 | 0.3390 | 3.476 | 1.102 | [12] |
| | 0.0703 | 0.3988 | 3.831 | 1.311 | [12] |
| | 0.0949 | 0.4793 | 4.338 | 1.621 | [12] |
| | 0.1905 | 0.6738 | 5.237 | 2.046 | [12] |
| | 0.3852 | 0.8462 | 5.247 | 1.635 | [12] |
| | 0.6010 | 0.9297 | 4.682 | 0.866 | [12] |
| | 0.7966 | 0.9717 | 4.159 | 0.241 | [12] |
| | 0.8957 | 0.9870 | 4.166 | 0.184 | [13] |
| | 0.9184 | 0.9900 | 4.109 | 0.120 | [13] |
| | 0.9383 | 0.9926 | 4.074 | 0.079 | [13] |
| | 0.9621 | 0.9956 | 4.080 | 0.077 | [13] |
| | 0.9814 | 0.9979 | 4.033 | 0.025 | [13] |
| | 1 | 1 | 4.014 | | [13] |
| | 1 | 1 | 3.987 | | [12] |
| 3-mpy (**1**) + $H_2O$ (**2**) | 0.0271 | 0.1831 | 2.569 | 0.545 | [14] |
| | 0.0395 | 0.2488 | 2.958 | 0.761 | [14] |
| | 0.0494 | 0.2947 | 3.270 | 0.954 | [14] |
| | 0.0604 | 0.3408 | 3.492 | 1.056 | [14] |
| | 0.0735 | 0.3896 | 3.714 | 1.150 | [14] |
| | 0.1070 | 0.4908 | 4.275 | 1.448 | [14] |
| | 0.1987 | 0.6662 | 5.048 | 1.763 | [14] |
| | 0.2975 | 0.7732 | 5.208 | 1.644 | [14] |
| | 0.4507 | 0.8685 | 5.057 | 1.244 | [14] |
| | 0.6010 | 0.9238 | 4.741 | 0.784 | [14] |
| | 0.8048 | 0.9707 | 4.381 | 0.301 | [14] |
| | 0.8963 | 0.9859 | 4.300 | 0.134 | [13] |
| | 0.9245 | 0.9900 | 4.258 | 0.082 | [13] |
| | 0.9389 | 0.9920 | 4.216 | 0.034 | [13] |
| | 0.9595 | 0.9948 | 4.232 | 0.043 | [13] |
| | 0.9797 | 0.9975 | 4.234 | 0.038 | [13] |
| | 1 | 1 | 4.203 | | [13] |
| | 1 | 1 | 4.156 | | [14] |

**Table 1** continued

| System | Mole fraction of (1) | Compression fraction of (1) | Internal pressure × $10^{-8}$ (Pa) | Excess internal pressure × $10^{-8}$ (Pa) | Data source |
|---|---|---|---|---|---|
| 4-mpy (**1**) + $H_2O$ (**2**) | 0.0241 | 0.1681 | 2.546 | 0.548 | [15] |
| | 0.0393 | 0.2509 | 3.015 | 0.795 | [15] |
| | 0.0487 | 0.2953 | 3.271 | 0.932 | [15] |
| | 0.0587 | 0.3379 | 3.517 | 1.064 | [15] |
| | 0.0744 | 0.3969 | 3.817 | 1.206 | [15] |
| | 0.0958 | 0.4643 | 4.181 | 1.389 | [15] |
| | 0.1950 | 0.6647 | 5.069 | 1.740 | [15] |
| | 0.3957 | 0.8428 | 5.145 | 1.339 | [15] |
| | 0.5884 | 0.9212 | 4.816 | 0.799 | [15] |
| | 0.7957 | 0.9696 | 4.456 | 0.309 | [15] |
| | 0.9000 | 0.9865 | 4.310 | 0.148 | [13] |
| | 0.9159 | 0.9888 | 4.256 | 0.088 | [13] |
| | 0.9396 | 0.9921 | 4.243 | 0.066 | [13] |
| | 0.9567 | 0.9945 | 4.241 | 0.057 | [13] |
| | 0.9747 | 0.9968 | 4.203 | 0.014 | [13] |
| | 1 | 1 | 4.198 | | [13] |
| | 1 | 1 | 4.228 | | [15] |

straightforward. Indeed, the term "internal pressure" is rather confusing as it suggests a quantity directly related to the attraction and repulsion forces acting between molecules. Although $p_{\text{int}}$ is positive for the majority of liquids, it can be negative as well—the obvious examples are $H_2O$ and $D_2O$ at temperatures below those of their maximum density. Thus, the correlation: the stronger the attraction, the higher is the internal pressure, is undoubtedly false. Equation 2 clearly shows the reason: the sign of $p_{\text{int}}$ depends on the sign of $E$. However, features of the excess internal-pressure isotherms plotted in Fig. 3 may be combined with other characteristics of the systems, such as the phase properties and the association energies in the 1:1 complexes with water.

Phase properties of the systems monomethylpyridines + $H_2O$ and $D_2O$ have been thoroughly discussed by Schneider [8]. 2-, 3- and 4-methylpyridine are completely miscible with water, from the freezing point up to the boiling temperature, at atmospheric pressure. At high pressures, all three systems show miscibility gaps. The lowest pressure required to force the phase separation is ca. 120 MPa for the 3-methylpyridine–$H_2O$ system with mole fraction $x_1 = 0.068$ at $T \approx 353$ K. The pressures for the 4- and 2-methylpyridine systems are ca. 400 MPa and 440 MPa, respectively. Deuterium oxide changes the phase properties in a similar way as an increase in pressure. Binary systems $D_2O$ + 3- or 2-methylpyridine are partially immiscible at atmospheric pressure, with the lower critical solution temperatures ca. 313 K at $x_1 = 0.084$ and 363 K at $x_1 = 0.088$, respectively. Although 4-methylpyridine is completely miscible

**Table 2** Internal pressures in binary mixtures of 2,6-dimethylpyridine and 2,4,6-trimethylpyridine with $H_2O$ and their excess values at $T = 296.15\,K$

| System | Mole fraction of (1) | Compression fraction of (1) | Internal pressure $\times 10^{-8}$ (Pa) | Excess internal pressure $\times 10^{-8}$ (Pa) | Data source |
|---|---|---|---|---|---|
| 2,6-dmpy (**1**) + $H_2O$ (**2**) | 0.0127 | 0.1206 | 2.136 | 0.317 | [16] |
| | 0.0150 | 0.1403 | 2.199 | 0.336 | [16] |
| | 0.0270 | 0.2286 | 2.743 | 0.681 | [16] |
| | 0.0500 | 0.3600 | 3.629 | 1.271 | [16] |
| | 0.0699 | 0.4457 | 4.205 | 1.654 | [16] |
| | 0.1000 | 0.5431 | 4.820 | 2.049 | [16] |
| | 0.1399 | 0.6350 | 5.261 | 2.284 | [16] |
| | 0.2592 | 0.7892 | 5.483 | 2.158 | [16] |
| | 0.3993 | 0.8767 | 5.178 | 1.656 | [16] |
| | 0.5989 | 0.9411 | 4.654 | 0.987 | [16] |
| | 0.7983 | 0.9769 | 4.147 | 0.399 | [16] |
| | 1 | 1 | 3.800 | | [16] |
| 2,4,6-tmpy (**1**) + $H_2O$ (**2**) | 0.0010 | 0.0118 | 1.517 | −0.055 | [17] |
| | 0.0020 | 0.0233 | 1.550 | −0.047 | [17] |
| | 0.0028 | 0.0324 | 1.600 | −0.017 | [17] |
| | 0.0037 | 0.0424 | 1.656 | 0.017 | [17] |
| | 0.0050 | 0.0565 | 1.850 | 0.180 | [17] |
| | 0.2097 | 0.7596 | 5.483 | 2.286 | [17] |
| | 0.3097 | 0.8423 | 5.324 | 1.949 | [17] |
| | 0.3995 | 0.8879 | 5.085 | 1.610 | [17] |
| | 0.5009 | 0.9228 | 4.821 | 1.270 | [17] |
| | 0.6008 | 0.9472 | 4.559 | 0.956 | [17] |
| | 0.7002 | 0.9653 | 4.341 | 0.698 | [17] |
| | 0.8007 | 0.9795 | 4.104 | 0.430 | [17] |
| | 0.9019 | 0.9909 | 3.911 | 0.212 | [17] |
| | 1 | 1 | 3.718 | | [17] |

with $D_2O$ at atmospheric pressure, the demixing pressure, ca. 230 MPa, is lower than that for the system containing $H_2O$. The increased tendency to phase separation on the exchange of $H_2O$ by $D_2O$ in the mixtures is reflected in the excess internal pressures at $T = 296.15\,K$, although this temperature is reasonably below the lower consolute values.

Comparing pairwise the $p^E_{int}$ isotherms (Fig. 3), one can notice that the maxima for the mixtures with $D_2O$ are higher than those for their counterparts with $H_2O$. For the $H_2O$ systems, the maxima of $p^E_{int}$ increase in the following order: 3-mpy ≈ 4-mpy < 2-mpy < 2,6-dmpy. 2,4,6-trimethylpyride is partially immiscible with water at temperatures above 278.85 K [29], but the $p^E_{int}$ isotherm is virtually the same as for the mixture containing 2,6-dimethylpyridine in the amine-rich range of concentrations.

**Table 3** Internal pressures in binary mixtures of monomethylpyridines with $D_2O$ and their excess values at $T = 296.15\,K$

| System | Mole fraction of (1) | Compression fraction of (1) | Internal pressure × $10^{-8}$ (Pa) | Excess internal pressure × $10^{-8}$ (Pa) | Data source |
|---|---|---|---|---|---|
| 2-mpy (**1**) + $D_2O$ (**2**) | 0 | 0 | 1.025 | | [18] |
| | 0.0200 | 0.1480 | 2.134 | 0.641 | [18] |
| | 0.0404 | 0.2637 | 2.854 | 1.022 | [18] |
| | 0.0484 | 0.3020 | 2.957 | 1.014 | [18] |
| | 0.0593 | 0.3491 | 3.219 | 1.137 | [18] |
| | 0.0776 | 0.4172 | 3.793 | 1.513 | [18] |
| | 0.0995 | 0.4846 | 4.167 | 1.689 | [18] |
| | 0.1858 | 0.6601 | 5.289 | 2.298 | [18] |
| | 0.2958 | 0.7814 | 5.296 | 1.950 | [18] |
| | 0.4062 | 0.8534 | 5.309 | 1.752 | [18] |
| | 0.5002 | 0.8949 | 4.932 | 1.253 | [18] |
| | 0.5923 | 0.9252 | 4.840 | 1.073 | [18] |
| | 0.7044 | 0.9530 | 4.447 | 0.599 | [18] |
| | 0.7981 | 0.9711 | 4.322 | 0.420 | [18] |
| | 0.9008 | 0.9872 | 4.121 | 0.172 | [18] |
| | 1 | 1 | 3.986 | | [18] |
| 3-mpy (**1**) + $D_2O$ (**2**) | 0 | 0 | 1.060 | | [19,23] |
| | 0.0150 | 0.1068 | 1.615 | 0.221 | [20] |
| | 0.0296 | 0.1931 | 2.749 | 1.084 | [20] |
| | 0.0375 | 0.2342 | 2.987 | 1.193 | [20] |
| | 0.0523 | 0.3022 | 3.451 | 1.445 | [20] |
| | 0.0577 | 0.3246 | 3.118 | 1.041 | [20] |
| | 0.0789 | 0.4020 | 4.016 | 1.697 | [20] |
| | 0.1423 | 0.5656 | 4.668 | 1.837 | [20] |
| | 0.1987 | 0.6606 | 4.899 | 1.771 | [20] |
| | 0.3042 | 0.7743 | 5.099 | 1.615 | [20] |
| | 0.3910 | 0.8344 | 5.061 | 1.388 | [20] |
| | 0.6023 | 0.9224 | 4.708 | 0.760 | [20] |
| | 0.7867 | 0.9666 | 4.315 | 0.229 | [20] |
| | 1 | 1 | 4.190 | | [20] |
| 4-mpy (**1**) + $D_2O$ (**2**) | 0 | 0 | 1.025 | | [18] |
| | 0.0204 | 0.1391 | 1.882 | 0.426 | [21] |
| | 0.0397 | 0.2428 | 2.665 | 0.886 | [21] |
| | 0.0473 | 0.2781 | 2.768 | 0.880 | [21] |
| | 0.0587 | 0.3260 | 3.216 | 1.178 | [21] |
| | 0.0776 | 0.3949 | 3.694 | 1.442 | [21] |

**Table 3** continued

| System | Mole fraction of (1) | Compression fraction of (1) | Internal pressure × $10^{-8}$ (Pa) | Excess internal pressure × $10^{-8}$ (Pa) | Data source |
|---|---|---|---|---|---|
| | 0.1004 | 0.4640 | 3.947 | 1.480 | [21] |
| | 0.1853 | 0.6383 | 4.938 | 1.930 | [21] |
| | 0.2999 | 0.7687 | 5.072 | 1.659 | [21] |
| | 0.3944 | 0.8348 | 5.135 | 1.516 | [21] |
| | 0.4925 | 0.8827 | 4.979 | 1.211 | [21] |
| | 0.5993 | 0.9206 | 4.758 | 0.873 | [21] |
| | 0.6980 | 0.9472 | 4.526 | 0.558 | [21] |
| | 0.8046 | 0.9696 | 4.372 | 0.334 | [21] |
| | 0.8958 | 0.9852 | 4.293 | 0.207 | [21] |
| | 1 | 1 | 4.132 | | [21] |

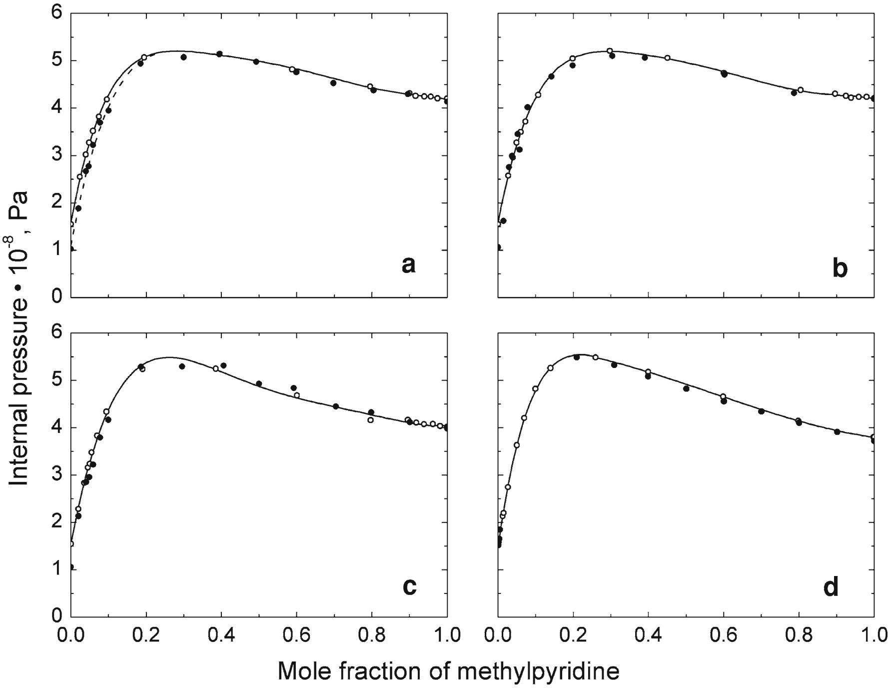

**Fig. 2** Internal pressure in binary mixtures of methylpyridines with water at $T = 296.15$ K as functions of the amine mole fraction $x_1$, points—experimental results, lines—interpolation: (**a**) 4-methylpyridine + $H_2O$ (●) or $D_2O$ (○); (**b**) 3-methylpyridine + $H_2O$ (●) or $D_2O$ (○); (**c**) 2-methylpyridine + $H_2O$ (●) or $D_2O$ (○); and (**d**) 2,6-dimethylpyridine (○) or 2,4,6-trimethylpyridine (●) + $H_2O$. Latter system shows a miscibility gap at $0.005 < x_1 < 0.2$

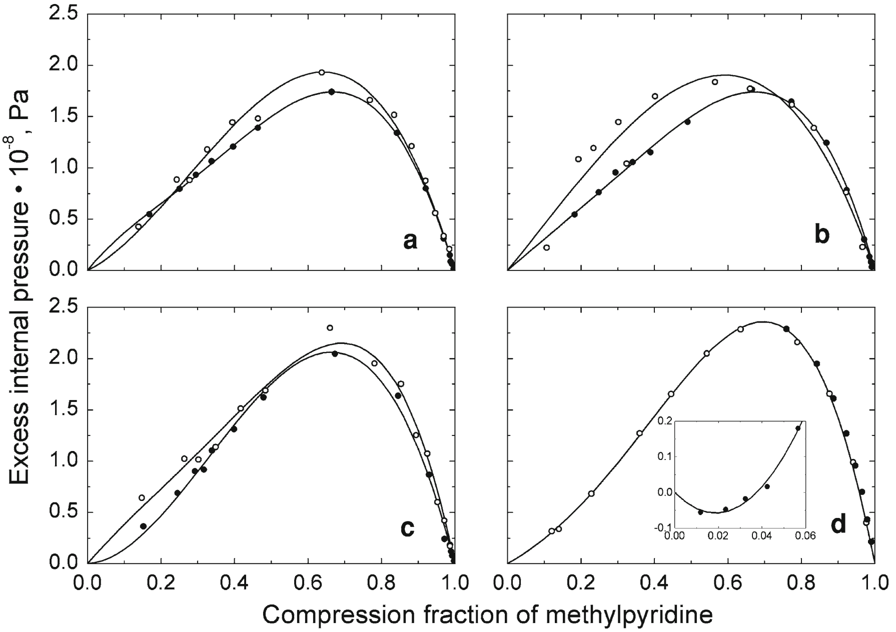

**Fig. 3** Excess internal pressure in binary mixtures of methylpyridines with water at $T = 296.15\,\text{K}$ as functions of the methylpyridine compression fraction $\psi_1$, points—experimental results, lines—polynomial interpolations (Eqs. 8 and 9): (**a**) 4-methylpyridine + $H_2O$ (●) or $D_2O$ (○); (**b**) 3-methylpyridine + $H_2O$ (●) or $D_2O$ (○); (**c**) 2-methylpyridine + $H_2O$ (●) or $D_2O$ (○); and (**d**) 2,6-dimethylpyridine (○) or 2,4,6-trimethylpyridine (●) + $H_2O$. Latter system shows a miscibility gap at $0.06 < \psi_1 < 0.75$

**Table 4** Coefficients of the Redlich–Kister polynomials (Eq. 8) approximating the excess internal pressure isotherms for binary mixtures of methylpyridine isomers with water

| System | $a_0$ | $a_1$ | $a_2$ | $\delta$ |
|---|---|---|---|---|
| 2-mpy + $H_2O$ | 7.01 ± 0.10 | −6.81 ± 0.27 | | 0.06 |
| 3-mpy + $H_2O$ | 6.00 ± 0.10 | −4.85 ± 0.17 | 1.99 ± 0.42 | 0.04 |
| 4-mpy + $H_2O$ | 5.98 ± 0.07 | −4.51 ± 0.13 | 1.93 ± 0.29 | 0.03 |
| 2,6-dmpy + $H_2O$ | 7.52 ± 0.06 | −8.18 ± 0.12 | 2.72 ± 0.24 | 0.03 |
| 2-mpy + $D_2O$ | 7.12 ± 0.22 | −6.37 ± 0.40 | 3.49 ± 0.91 | 0.09 |
| 3-mpy + $D_2O$ | 7.34 ± 0.29 | −2.95 ± 0.70 | | 0.20 |
| 4-mpy + $D_2O$ | 6.95 ± 0.12 | −5.15 ± 0.28 | | 0.07 |
| 2,4,6-tmpy + $H_2O$[a] | | −6.13 ± 0.60 | 163.41 ± 12.74 | 0.01 |

[a] Coefficients of Eq. 9 valid for dilute solutions of 2,4,6-trimethylpyridine; $\delta$—mean deviation from the regression line

Thus, the substitution of the $CH_3$ group in the *ortho* position towards the nitrogen atom in the pyridine ring causes a significant increase of the $p_{\text{int}}^{\text{E}}$ maximum. The *ortho* effect, consisting of the changes of the hydrogen bond energy, unspecific interactions with a steric hindrance, and changes in resonance interactions has been observed in numerous systems [30]. For the investigated mixtures, the *ortho* effect is manifested

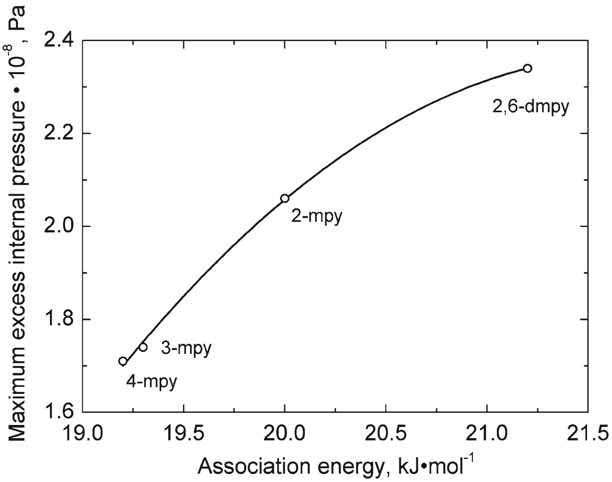

**Fig. 4** Correlation of the maximum excess internal pressures obtained in this study with the association energies: (○) 1:1 water–methylpyridine complexes reported in the literature [4]

mainly in the strengthening of the O–H· · ·N bonds. The molecule of water is small, and its proton can easily reach the nitrogen atom of the pyridine ring in spite of the neighboring $CH_3$ groups. That is confirmed by theoretically calculated association energies of the 1:1 complexes of methylpyridines with $H_2O$. The energies are: (19.2, 19.3, 20.0, and 21.2) $\text{kJ} \cdot \text{mol}^{-1}$ for 4-methylpyridine, 3-methylpyridine, 2-methylpyridine, and 2,6-dimethylpyridine, respectively [4]. This series remains in perfect agreement with that of the maximum $p_{\text{int}}^{\text{E}}$ values, which is illustrated by Fig. 4.

The above considerations may be summed up in the following way. $CH_3$ groups substituted in *ortho* positions in the pyridine ring increase the energy of the water–amine hydrogen bonds. A similar increase, although smaller, is caused by the exchange of $H_2O$ by $D_2O$ in the mixture. As was mentioned in Sect. 1, a nitrogen atom in the pyridine ring is an ca. 30 % stronger acceptor of protons than the oxygen atom in a water molecule [1]. Most probably, the difference in energy between the O–D· · ·N and O–D· · ·O bonds is higher than that between the O–H· · ·N and O–H· · ·O ones. Thus, the deviation from the thermodynamically ideal behavior for the $D_2O$ mixtures is larger than that for the $H_2O$ ones. The excess internal-pressure approach makes it possible to emphasize this difference.

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