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# Determination of Infinite Dilution Partial Molar Excess Enthalpies and Volumes for Some Ionic Liquid Precursors in Water and Methanol Using Tandem Flow Mixing Calorimetry and Vibrating-Tube Densimetry

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**ABSTRACT:** A flow mixing microcalorimetric system we developed recently was appended in this work with a vibrating tube densimeter into a tandem flow arrangement. This new combined apparatus (calo/densimeter) allows simultaneous automatic measurement of mixing enthalpies and densities of highly dilute solutions as a function of composition and, in turn, reliable determination of the solute's infinite dilution partial molar excess enthalpies $\overline{H}_1^{E,\infty}$ and volumes $\overline{V}_1^{E,\infty}$. The performance of the calo/densimeter was verified using 1-propanol in water, and then the apparatus was employed to determine $\overline{H}_1^{E,\infty}$ and $\overline{V}_1^{E,\infty}$ of several ionic liquid precursors (*N*-methylimidazole, *N*-methylpiperidine, *N*-methylmorpholine, 2-picoline, 3-picoline, and 2,6-lutidine) in water and methanol at 298.15 K. The changes of enthalpy associated with solvation and the transfer of the solutes from water to methanol were evaluated. The thermodynamic behavior observed for individual solutes was compared and briefly discussed in terms of molecular interactions.

## 1. INTRODUCTION

Heterocyclic nitrogen bases are important biochemical building blocks and indispensable reagents for organic synthesis. In respective processes these substances often interact with various solvent media. Their solutions in water and other protic solvents exhibit particularly complex structures and often also peculiar behavior, thus attracting the interest of both experimentalists and theoreticians.[1−12] In this work we deal with six selected heterocyclic nitrogen bases that serve as precursors for ionic liquids, namely, 1-methylimidazole, 1-methylpiperidine, *N*-methylmorpholine, 3-methylpyridine (3-picoline), 4-methylpyridine (4-picoline), and 2,6-dimethylpyridine (2,6-lutidine). Their structural formulas are shown in Figure 1. For these substances we present here accurate measurements of their infinite dilution partial molar excess enthalpies $\overline{H}_1^{E,\infty}$ and volumes $\overline{V}_1^{E,\infty}$ in water and methanol for which a new tandem flow setup of isothermal mixing microcalorimeter and a vibrating-tube densimeter was used.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** *N*-Methylimidazole (≥ 0.99, redistilled), *N*-methylpiperidine (0.99), *N*-methylmorpholine (0.995+, redistilled), 3-picoline (0.995+), 4-picoline (0.99), and 2,6-lutidine (≥ 0.99, redistilled) used as solutes were all obtained from Sigma-Aldrich. Their declared purity was verified by gas chromatography using a DB-WAX capillary column. Water contents as determined by Fischer titration did not exceed 0.0004 mass fraction. Methanol (puriss, anhydrous) was obtained from Merck. Water was distilled and subsequently treated by a Milli-Q Water Purification System (Millipore, USA). Before measurements, all liquids were partially degassed by vacuum filtration and sonification.

**2.2. Apparatus and Procedure.** A refined isothermal mixing microcalorimeter described previously[13] was appended in this work by a vibrating-tube densimeter into a tandem flow arrangement, and this combined instrument (calo/densimeter) was used to measure simultaneously mixing enthalpies $H^E$ and densities of highly dilute solutions as a function of solute mole fraction and the infinite dilution partial molar excess enthalpy $\overline{H}_1^{E,\infty}$ and volume $\overline{V}_1^{E,\infty}$ being in turn determined by reliable extrapolation of these data. A schematic diagram of this calo/densimeter assembly with a fully automatic control of the entire experimental sequence is given in Figure 2. The setup consists of a modified model 4400 isothermal differential heat conduction microcalorimeter (CSC, Provo, USA) equipped with flow mixing cells and a highly asymmetric pumping system capable of delivering accurately very small mass flow rates of one component. The calorimeter is characterized by a thermal power sensitivity of 0.1 $\mu$W and a time constant of 300 s. The pumping system is composed of two high-quality syringe pumps, a model HPP 5001 of 400 mL capacity from Laboratorní Přístroje (Praha, Czech Republic) and a model PHD 2000 from Harvard Apparatus (Holliston, MA, USA) equipped with a 8 mL stainless steel syringe. The vibrating-tube densimeter Anton Paar model DMA 5000 is characterized by a sensitivity $1 \cdot 10^{-6}$ $g \cdot cm^{-3}$. It was attached to the outlet tube from the calorimeter directly at its exit from the head air thermostatting box of the calorimeter and the connection was thermally insulated. The uncertainty of the absolute setting of experimental temperature of the calorimeter and the densimeter is estimated to be 10 mK.

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The present measurements were conducted at the solvent flow rate of 0.1 mL·min$^{-1}$ and solute flow rates selected typically from the range (3 to 0.4) $\mu$L·min$^{-1}$ so that sufficient dilution was attained. The densimeter signal was proved to be independent of the total flow, being the same as for a stagnant medium. The signals from the calorimeter and the densimeter were recorded at each composition for 5 h. The baseline was recorded for 3 h, as both the initial and the final step of the experimental run. A typical run examining six compositions in the range of solute mole fraction $x_1$ from (0.007 down to 0.001) thus lasted 36 h. Signals corresponding to mixtures were averaged over integral multiples of the rotation period of the solute pump screw to compensate for mechanical imperfections of the pump. Figures 3 and 4 show examples of the signals from the calorimeter and the densimeter, respectively, as recorded in an experimental run for 1-methylimidazole in water. The calorimetric signal was calibrated using a Joule effect produced by a built-in calibration heater on the pure solvent (water or methanol). The calibration of the densimeter was performed using water and methanol whose densities were taken from the literature.[14,15] In addition, ad hoc single-fluid calibrations of the densimeter were carried out at each run using baseline signal corresponding to the pure solvent (water or methanol). The infinite dilution partial molar excess enthalpy $\overline{H}_1^{\mathrm{E},\infty}$ and volume $\overline{V}_1^{\mathrm{E},\infty}$ were determined by linear extrapolation of the quantity $H^{\mathrm{E}}/(x_1x_2)$ and $V^{\mathrm{E}}/(x_1x_2)$, respectively, as functions of $x_1$ to infinite dilution. The corresponding plots are exemplified in Figures 5 and 6.

The performance of our calo/densimeter instrument was verified on the 1-propanol in water system. The measured value of infinite dilution partial molar excess enthalpy at 298.15 K, $\overline{H}_1^{\mathrm{E},\infty} = -10.12$ kJ·mol$^{-1}$, matches exactly the one obtained previously[13] and is in excellent agreement with the recommendation ($-10.16$ kJ·mol$^{-1}$).[16,17] The measured value of infinite dilution partial molar volume at 298.15 K, $\overline{V}_1^{\infty} = 70.79$ cm$^3$·mol$^{-1}$, also compares favorably with the results from the literature (70.88;[18] 70.63;[19] 70.60;[20] 70.70[21]) cm$^3$·mol$^{-1}$.

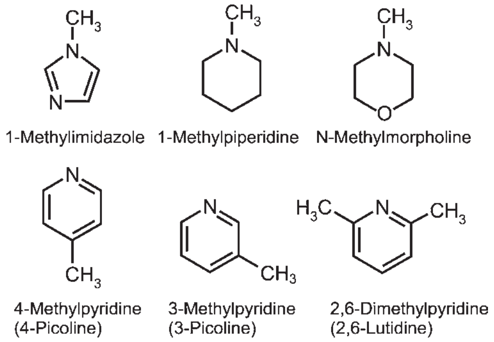

**Figure 1.** Structural formulas and names of solutes studied.

## 3. RESULTS AND DISCUSSION

Densities of pure solutes at 298.15 K were measured first to check solute purity and provide reliable data for the determination of the composition of pumped streams and evaluation of excess volumes. For 1-methylpiperidine, the density was determined at five temperatures in the range from (288.15 to 308.15) K, since the only temperature-dependent measurement recently reported by Coulier et al.[22] appears to be considerably scattered. The measured densities of pure solutes and their comparison to literature values are given in Table 1. The combined standard uncertainty of pure solute densities determined in this work is estimated to be $2 \cdot 10^{-4}$ g·cm$^{-3}$.

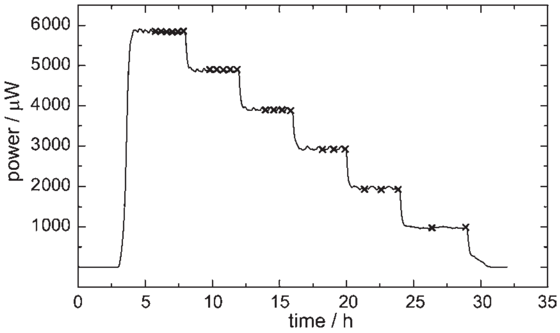

**Figure 3.** Calorimetric signal for a typical experimental run: 1-methylimidazole in water, —, signal; ×, pump period mark.

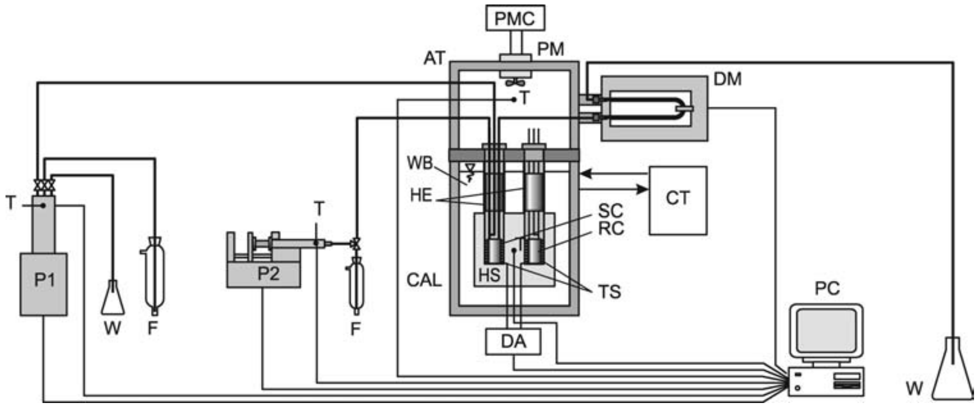

**Figure 2.** Schematic diagram of the tandem flow arrangement of the isothermal mixing microcalorimeter and the vibrating-tube densimeter: AT, air thermostat; CAL, microcalorimeter; CT, cooling thermostat; DA, differential amplifier; DM, vibrating-tube densimeter; F, feed bottle; HE, heat exchanger; HS, heat sink; P1, high-performance liquid chromatography (HPLC) syringe pump (400 mL); P2, syringe pump (8 mL); PC, computer for data acquisition and setup control; PM, Peltier cooler/heater module with fan; PMC, Peltier module controller; RC, reference cell; SC, sample cell; T, temperature sensor; TS, thermoelectric sensors; W, waste bottle; WB, ultra stable thermostatting water bath.

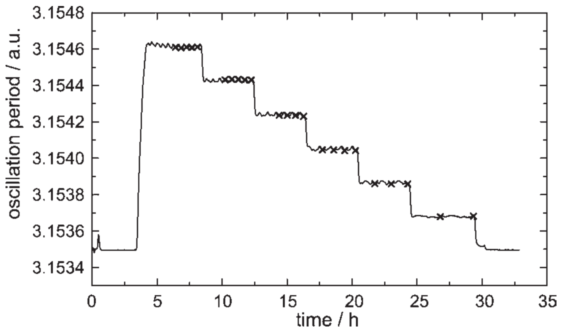

**Figure 4.** Densimetric signal for a typical experimental run: 1-methylimidazole in water, —, signal; ×, pump period mark.

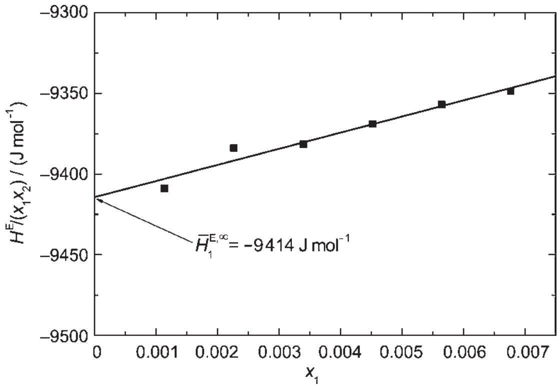

**Figure 5.** Extrapolation of measured excess enthalpy data to in finite dilution: 1-methylimidazole in water, ■, measured values; —, linear fit.

Primary experimental excess enthalpy and density data for dilute solutions of nitrogen bases in water and methanol obtained in this work are summarized in Table 2. On the basis of statistical analysis of replicated measurements, the standard uncertainty for excess enthalpy determinations was estimated to be 0.4 % and that for density determinations $5 \cdot 10^{-6}$ g·cm$^{-3}$, except for 1-methylpiperidine + water, *N*-methylmorpholine + methanol, and 3-picoline + methanol for which the latter value is $1 \cdot 10^{-5}$ g·cm$^{-3}$. The inferred infinite dilution partial molar properties of studied solutes in water and methanol are given in Tables 3 and 4. Each reported infinite dilution value corresponds to the average of at least two replicated measurements. The standard uncertainties estimated using the error propagation law comprise contributions from all possible sources of error. The value of $\bar{H}_1^{E,\infty}$ given for 1-methylpiperidine (p$K_a$ = 10.08) in water was corrected for hydrolysis of this solute as described by Cabani et al.[2] The correction increased the observed exothermic effect by about 3 %. For other studied solutes (5.68 < p$K_a$ < 7.4), the effect of hydrolysis was found to be negligible. A comparison of measured values of $\bar{H}_1^{E,\infty}$ to existing literature data in Table 3 shows very good agreement except for older measurements of Sacconi et al.[1] for 3-picoline and 2,6-lutidine which are about 5 % more exothermic than the present values. For $\bar{V}_1^{E,\infty}$ results in Table 4, no similar comparison is presented; even though $V^E$ measurements in the entire composition range for some of the systems studied here have been reported in the literature,[5,11,30] their extrapolation to obtain infinite dilution values is unreliable and cannot be justified.

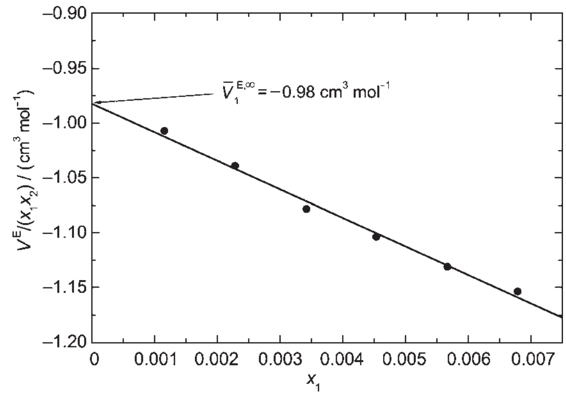

**Figure 6.** Extrapolation of measured excess volume data to infinite dilution: 1-methylimidazole in water, ●, measured values; —, linear fit.

### Table 1. Experimental Densities of Pure Solutes $\rho$ and Their Comparison with Literature Values

| substance | $T$/K | $\rho$/(g·cm$^{-3}$) | | |
|---|---|---|---|---|
| | | this work | lit. | ref |
| 1-methylimidazole | 298.15 | 1.03114 | 1.0316 | 23 |
| 1-methylpiperidine[a] | 288.15 | 0.82153 | 0.82224 | 22 |
| | 293.15 | 0.81722 | 0.8157 | 24 |
| | 298.15 | 0.81262 | 0.81089 | 22 |
| | 303.15 | 0.80816 | | |
| | 308.15 | 0.80361 | 0.80385 | 22 |
| *N*-methylmorpholine | 298.15 | 0.91415 | 0.91406 | 25 |
| 3-picoline | 298.15 | 0.95261 | 0.95197 | 26 |
| 4-picoline | 298.15 | 0.94987 | 0.94982 | 27 |
| 2,6-lutidine | 298.15 | 0.91819 | 0.91845 | 5 |
| | | | 0.91811 | 28 |

[a] The equation $\rho$/(g·cm$^{-3}$) = 1.08032 − 8.978·10$^{-4}$ ($T$/K) fits the present data with a standard deviation of 8·10$^{-5}$ g·cm$^{-3}$.

As seen from Tables 3 and 4, the dissolution of all studied solutes in both water and methanol is strongly exothermic and accompanied with volume contraction. This fact convincingly indicates appreciable solute−solvent complex formation. The complexes are formed by hydrogen bonding of the solvent proton to the electron lone pair of the solute nitrogen atom. In case of 1-methylimidazole, the lone pair of the pyridine-like nitrogen is unambiguously its basic site.[29] The strongest complexation appears to occur between 1-methylpiperidine or *N*-methylmorpholine and water, the two solute−solvent pairs for which the most pronounced dissolution effects were observed.

In Table 5, we give enthalpies of solute transfer from the gas state to the infinitely dilute solution (solvation enthalpies $\Delta_{solv}H_1$) and from the aqueous solution to the methanolic solution at infinite dilution $\Delta_{tr}H^{\infty}$. Values of standard vaporization enthalpies $\Delta_{vap}H_1°$ of pure solutes taken from the literature and used in the evaluation of the solvation enthalpies are also listed. For all solutes studied the transfer enthalpy from water to methanol is positive. The solute transfer from water to methanol is energetically unfavorable in spite of that the energy penalty to

Table 2. Primary Experimental Excess Enthalpy $H^{E}$ and Density $\rho$ Data[a] for Dilute Solutions of Nitrogen Bases in Water and Methanol at $T$ = 298.15 K

|  | $H^{E}$ | $\rho$ |  | $H^{E}$ | $\rho$ |
|---|---|---|---|---|---|
| $x_1$ | $\mathrm{J\cdot mol^{-1}}$ | $\mathrm{g\cdot cm^{-3}}$ | $x_1$ | $\mathrm{J\cdot mol^{-1}}$ | $\mathrm{g\cdot cm^{-3}}$ |
| 1-Methylimidazole (1) + Water (2) |  |  |  |  |  |
| 0.006766 | −62.61 | 0.998483 | 0.006765 | −62.85 | 0.998459 |
| 0.005644 | −52.40 | 0.998246 | 0.005642 | −52.53 | 0.998222 |
| 0.004520 | −42.03 | 0.997986 | 0.004518 | −42.17 | 0.997985 |
| 0.003394 | −31.67 | 0.997750 | 0.003392 | −31.74 | 0.997750 |
| 0.002265 | −21.14 | 0.997514 | 0.002264 | −21.21 | 0.997513 |
| 0.001134 | −10.62 | 0.997281 | 0.001133 | −10.66 | 0.997279 |
| 1-Methylpiperidine (1) + Water (2) |  |  |  |  |  |
| 0.004409 | −129.62 | 0.994716 | 0.004398 | −128.90 | 0.994752 |
| 0.003675 | −108.36 | 0.995081 | 0.003666 | −107.86 | 0.995109 |
| 0.002942 | −86.15 | 0.995470 | 0.002934 | −86.17 | 0.995483 |
| 0.002208 | −64.46 | 0.995862 | 0.002202 | −64.55 | 0.995866 |
| 0.001473 | −42.80 | 0.996260 | 0.001470 | −42.81 | 0.996261 |
| 0.000737 | −21.41 | 0.996658 | 0.000735 | −21.29 | 0.996660 |
| 0.004404 | −129.19 | 0.994733 |  |  |  |
| 0.003671 | −107.93 | 0.995097 |  |  |  |
| 0.002939 | −86.10 | 0.995482 |  |  |  |
| 0.002206 | −64.90 | 0.995858 |  |  |  |
| 0.001471 | −43.12 | 0.996253 |  |  |  |
| 0.000736 | −21.46 | 0.996651 |  |  |  |
| *N*-Methylmorpholine (1) + Water (2) |  |  |  |  |  |
| 0.004858 | −139.88 | 0.997188 | 0.004854 | −140.03 | 0.997187 |
| 0.004050 | −116.89 | 0.997153 | 0.004048 | −116.77 | 0.997151 |
| 0.003242 | −93.78 | 0.997121 | 0.003242 | −93.68 | 0.997121 |
| 0.002434 | −70.34 | 0.997094 | 0.002433 | −70.55 | 0.997095 |
| 0.001624 | −47.12 | 0.997074 | 0.001623 | −47.26 | 0.997074 |
| 0.000813 | −23.62 | 0.997058 | 0.000812 | −23.65 | 0.997058 |
| 3-Picoline (1) + Water (2) |  |  |  |  |  |
| 0.005509 | −51.22 | 0.996980 | 0.005507 | −51.07 | 0.996982 |
| 0.004594 | −43.22 | 0.996989 | 0.004592 | −42.96 | 0.996991 |
| 0.003678 | −34.85 | 0.996998 | 0.003677 | −34.65 | 0.996999 |
| 0.002761 | −26.32 | 0.997007 | 0.002760 | −26.19 | 0.997008 |
| 0.001842 | −17.66 | 0.997017 | 0.001842 | −17.57 | 0.997018 |
| 0.000922 | −8.92 | 0.997030 | 0.000922 | −8.88 | 0.997031 |
| 4-Picoline (1) + Water (2) |  |  |  |  |  |
| 0.005492 | −52.02 | 0.996939 | 0.005492 | −52.09 | 0.996939 |
| 0.004580 | −43.80 | 0.996955 | 0.004580 | −43.77 | 0.996956 |
| 0.003668 | −35.32 | 0.996971 | 0.003667 | −35.29 | 0.996972 |
| 0.002754 | −26.79 | 0.996988 | 0.002753 | −26.77 | 0.996988 |
| 0.001837 | −18.06 | 0.997005 | 0.001837 | −17.97 | 0.997005 |
| 0.000919 | −9.07 | 0.997023 | 0.000919 | −9.05 | 0.997024 |
| 2,6-Lutidine (1) + Water (2) |  |  |  |  |  |
| 0.004615 | −72.43 | 0.996644 | 0.004618 | −72.36 | 0.996644 |
| 0.003847 | −60.41 | 0.996685 | 0.003851 | −60.34 | 0.996684 |
| 0.003080 | −48.05 | 0.996732 | 0.003083 | −48.06 | 0.996734 |
| 0.002312 | −35.79 | 0.996792 | 0.002314 | −35.97 | 0.996791 |
| 0.001543 | −23.65 | 0.996862 | 0.001544 | −23.74 | 0.996861 |
| 0.000772 | −11.61 | 0.996946 | 0.000773 | −11.74 | 0.996945 |
| 1-Methylimidazole (1) + Methanol (2) |  |  |  |  |  |
| 0.015099 | −104.20 | 0.794617 | 0.015095 | −104.10 | 0.794633 |
| 0.012614 | −87.19 | 0.793304 | 0.012613 | −87.09 | 0.793323 |
| 0.010117 | −69.96 | 0.791972 | 0.010117 | −69.89 | 0.791975 |
| 0.007607 | −52.54 | 0.790606 | 0.007607 | −52.62 | 0.790615 |
| 0.005084 | −35.06 | 0.789231 | 0.005084 | −35.17 | 0.789234 |
| 1-Methylpiperidine (1) + Methanol (2) |  |  |  |  |  |
| 0.009904 | −100.02 | 0.788454 | 0.009900 | −100.49 | 0.788458 |
| 0.008266 | −83.94 | 0.788139 | 0.008264 | −84.22 | 0.788141 |
| 0.006624 | −67.52 | 0.787816 | 0.006622 | −67.78 | 0.787816 |
| 0.004976 | −50.96 | 0.787486 | 0.004975 | −51.13 | 0.787488 |
| 0.003323 | −34.04 | 0.787150 | 0.003322 | −34.25 | 0.787153 |
| 0.001664 | −17.24 | 0.786815 | 0.001664 | −17.18 | 0.786815 |
| *N*-Methylmorpholine (1) + Methanol (2) |  |  |  |  |  |
| 0.010911 | −63.66 | 0.791753 | 0.010904 | −63.63 | 0.791711 |
| 0.009108 | −53.61 | 0.790908 | 0.009104 | −53.37 | 0.790862 |
| 0.007299 | −43.15 | 0.790044 | 0.007298 | −43.01 | 0.790004 |
| 0.005484 | −32.51 | 0.789159 | 0.005484 | −32.28 | 0.789119 |
| 0.003663 | −21.76 | 0.788267 | 0.003662 | −21.72 | 0.788239 |
| 0.001834 |  | 0.787377 | 0.001834 |  | 0.787359 |
| 3-Picoline (1) + Methanol (2) |  |  |  |  |  |
| 0.012325 | −56.30 |  | 0.012323 | −56.28 | 0.791892 |
| 0.010293 | −47.32 | 0.791057 | 0.010293 | −47.18 | 0.791007 |
| 0.008251 | −38.16 | 0.790158 | 0.008253 | −37.87 | 0.790117 |
| 0.006201 | −28.60 | 0.789240 | 0.006203 | −28.51 | 0.789213 |
| 0.004143 | −19.11 | 0.788320 | 0.004144 | −19.05 | 0.788293 |
| 0.002075 |  | 0.787397 |  |  |  |
| 4-Picoline (1) + Methanol (2) |  |  |  |  |  |
| 0.012316 | −61.15 | 0.791924 | 0.012312 | −61.25 | 0.791923 |
| 0.010284 | −51.59 | 0.791066 | 0.010282 | −51.33 | 0.791039 |
| 0.008244 | −41.45 | 0.790152 | 0.008243 | −41.35 | 0.790150 |
| 0.006195 | −31.20 | 0.789246 | 0.006195 | −31.27 | 0.789247 |
| 0.004139 | −20.76 | 0.788319 | 0.004138 | −20.84 | 0.788325 |
| 2,6-Lutidine (1) + Methanol (2) |  |  |  |  |  |
| 0.010356 | −79.60 | 0.791414 | 0.010353 | −79.46 | 0.791405 |
| 0.008647 | −66.53 | 0.790625 | 0.008643 | −66.59 | 0.790602 |
| 0.006929 | −53.25 | 0.789802 | 0.006928 | −53.44 | 0.789788 |
| 0.005206 | −40.05 | 0.788971 | 0.005205 | −40.17 | 0.788964 |
| 0.003476 | −26.67 | 0.788131 | 0.003476 | −26.80 | 0.788126 |
| 0.001741 | −13.44 |  | 0.001741 | −13.35 |  |

[a] Relative standard uncertainty of excess enthalpy data $s_{\mathrm{rel}}(H^{E}) = 0.004$, standard uncertainty of density data $s(\rho) = 5\cdot10^{-6}\ \mathrm{g\cdot cm^{-3}}$, except for 1-methylpiperidine + water, *N*-methylmorpholine + methanol, and 3-picoline + methanol for which $s(\rho) = 1\cdot10^{-5}\ \mathrm{g\cdot cm^{-3}}$. Densities of solutions refer to pure solvent densities 0.997050 $\mathrm{g\cdot cm^{-3}}$ and 0.786470 $\mathrm{g\cdot cm^{-3}}$ for water and methanol, respectively, at 298.15 K used to calibrate the densimeter.

form a cavity for incorporating the solute molecule in the solvent medium is for water much greater than for methanol. This means that methanol is less efficient proton donor than water, a fact supported also by previous studies.[7,29,35] Consistent with it is also the volume change upon solute transfer from water to methanol which is for all solutes except 1-methylimidazole positive.

In Figure 7 the solvation enthalpies from Table 5 are plotted against the Abraham hydrogen bond basicity parameter[36] of the solutes. As seen, the observed hydration enthalpies correlate well with the solute hydrogen bond basicity; however, solvation enthalpies of 1-methylpiperidine and *N*-methylmorpholine in methanol break an analogous pattern for this solvent, probably because the hydrogen bonding of methanol to these solutes is sterically hindered. On the other hand, two methyl groups in ortho position of 2,6-lutidine do not hinder the formation of hydrogen bonds with water or methanol, but on the contrary due to the induction effect of these groups on the nitrogen atom they strengthen the hydrogen bonding (compare the dissolution effects observed for 3-picoline or 4-picoline to those for

**Table 3. Experimental Limiting Partial Molar Excess Enthalpies $\bar{H}_1^{E,\infty}$ of Nitrogen Bases at Infinite Dilution in Water and Methanol at $T$ = 298.15 K and Their Standard Uncertainties $s(\bar{H}_1^{E,\infty})$**

| solute | $\bar{H}_1^{E,\infty}$ kJ·mol$^{-1}$ | $s(\bar{H}_1^{E,\infty})$ kJ·mol$^{-1}$ | ref | $\bar{H}_1^{E,\infty}$ kJ·mol$^{-1}$ | $s(\bar{H}_1^{E,\infty})$ kJ·mol$^{-1}$ | ref |
|---|---|---|---|---|---|---|
| | Water | | | Methanol | | |
| 1-methylimidazole | −9.40 | 0.06 | | −6.92 | 0.05 | |
| | −9.41 | 0.42 | 7 | −7.07 | 0.25 | 7 |
| | −9.75 | 0.13 | 29 | −6.86 | 0.25 | 29 |
| 1-methylpiperidine | −30.08 | 0.15 | | −10.38 | 0.04 | |
| | −30.0 | 0.46 | 2 | | | |
| *N*-methylmorpholine | −29.16 | 0.10 | | −5.99 | 0.03 | |
| | −29.29 | 0.17 | 3 | | | |
| 3-picoline | −9.71 | 0.05 | | −4.62 | 0.02 | |
| | −10.17 | 0.06 | 1 | | | |
| 4-picoline | −9.95 | 0.05 | | −5.08 | 0.02 | |
| | −10.19 | 0.06 | 1 | | | |
| 2,6-lutidine | −15.10 | 0.09 | | −7.69 | 0.03 | |
| | −15.90 | 0.06 | 1 | | | |

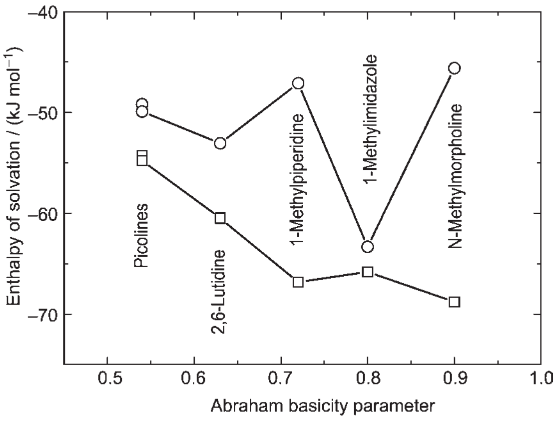

**Figure 7.** Enthalpy of solvation of the studied heterocyclic nitrogen bases in water and methanol plotted against Abraham hydrogen bond basicity parameter of the solute. □, water; ○, methanol.

**Table 4. Experimental Limiting Partial Molar Volumes $\bar{V}_1^{\infty}$ and Excess Volumes $\bar{V}_1^{E,\infty}$ of Nitrogen Bases at Infinite Dilution in Water and Methanol at $T$ = 298.15 K and Their Standard Uncertainties $s(\bar{V}) = s(\bar{V}_1^{\infty}) = s(\bar{V}_1^{E,\infty})$**

| solute | $\bar{V}_1^{\infty}$ cm$^3$·mol$^{-1}$ | $\bar{V}_1^{E,\infty}$ cm$^3$·mol$^{-1}$ | $s(\bar{V})$ cm$^3$·mol$^{-1}$ | $\bar{V}_1^{\infty}$ cm$^3$·mol$^{-1}$ | $\bar{V}_1^{E,\infty}$ cm$^3$·mol$^{-1}$ | $s(\bar{V})$ cm$^3$·mol$^{-1}$ |
|---|---|---|---|---|---|---|
| | | Water | | | Methanol | |
| 1-methylimidazole | 78.65 | −0.98 | 0.03 | 76.12 | −3.51 | 0.05 |
| 1-methylpiperidine | 109.20 | −12.84 | 0.15 | 115.34 | −6.70 | 0.03 |
| *N*-methylmorpholine | 101.25 | −9.40 | 0.05 | 103.25 | −7.40 | 0.25 |
| 3-picoline | 93.74 | −4.02 | 0.03 | 95.40 | −2.36 | 0.10 |
| 4-picoline | 93.86 | −4.18 | 0.03 | 95.06 | −2.98 | 0.05 |
| 2,6-lutidine | 109.98 | −6.72 | 0.03 | 111.46 | −5.24 | 0.05 |

**Table 5. Vaporization Enthalpies of Pure Solutes $\Delta_{vap}H_1°$, Their Solvation Enthalpies[a] $\Delta_{solv}H_1$ in Water and Methanol, and Their Transfer Enthalpies $\Delta_{tr}H^{\infty}$ from the Aqueous Solution to the Methanolic Solution at Infinite Dilution and $T$ = 298.15 K along with Respective Standard Uncertainties**

| solute | $\Delta_{vap}H_1°$ kJ·mol$^{-1}$ | $s(\Delta_{vap}H_1°)$ kJ·mol$^{-1}$ | ref | $\Delta_{solv}H_1$ kJ·mol$^{-1}$ | $s(\Delta_{solv}H_1)$ kJ·mol$^{-1}$) | $\Delta_{solv}H_1$ kJ·mol$^{-1}$ | $s(\Delta_{solv}H_1)$ kJ·mol$^{-1}$ | $\Delta_{tr}H^{\infty}(w \rightarrow m)$ kJ·mol$^{-1}$ | $s(\Delta_{tr}H^{\infty})$ kJ·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Water | | Methanol | | | |
| 1-methylimidazole | 56.40 | 1.1 | 31 | −65.80 | 1.1 | −63.31 | 1.1 | 2.49 | 0.08 |
| 1-methylpiperidine | 36.72 | 0.08 | 32 | −66.82 | 0.17 | −47.10 | 0.09 | 19.72 | 0.16 |
| *N*-methylmorpholine | 39.62 | 0.26 | 33 | −68.78 | 0.28 | −45.61 | 0.26 | 23.17 | 0.10 |
| 3-picoline | 44.57 | 0.22 | 34 | −54.28 | 0.22 | −49.19 | 0.22 | 5.09 | 0.05 |
| 4-picoline | 44.83 | 0.22 | 34 | −54.78 | 0.22 | −49.91 | 0.22 | 4.87 | 0.05 |
| 2,6-lutidine | 45.38 | 0.23 | 34 | −60.48 | 0.23 | −53.07 | 0.23 | 7.41 | 0.09 |

[a] $\Delta_{solv}H_1 = \bar{H}_1^{E,\infty} - \Delta_{vap}H_1°$.

2,6-lutidine). This conclusion has been reached previously by Marczak and co-workers.[9,10,12]

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