

THE ENTHALPIES OF DILUTION OF PYRIDINE AND METHYLPYRIDINE AT 298.15 K

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The enthalpies of dilution of aqueous solutions for pyridine and methylpyridine isomers have been determined with a 2277-Thermal Activity Monitor at 298.15 K. The results have been treated using the excess function concept and homotactic interaction coefficients have been obtained. The homotactic enthalpic pairwise interaction coefficients are discussed qualitatively in terms of substitution effects of methyl group introduced into the pyridine ring.

Keywords: homotactic enthalpic pairwise interaction coefficient, hydrated solute species, methylpyridine, pyridine

Introduction

There is currently a considerable amount of interest, much of which is driven by problems in molecular biology and environmental science, in the ‘non-bonding’ interactions that occur in condensed media. Heterocyclic compounds exist extensively in nature, such as in the chlorophyll of plants and hemochrome of animals. Thus, the importance of studying the thermodynamic properties of heterocyclic compounds is apparent; however, the great structural diversity of heterocycles makes this a daunting challenge. Pyridine and methylpyridine, typical tertiary heterocyclic amines, seem to be particularly suited for this kind of study because pyridine derivatives afford a series of homologous and isomeric variations with respect to the molecular structure and behavior in physical and chemical properties [1]. Many alkaloids and important natural products contain a pyridine ring or hydrogenized pyridine ring structure [2]. Methylpyridine, generally called picoline, is a kind of compound of the most significance among the derivatives of pyridine. They are all very important organic synthesis materials, applied in the fields of medicine, pesticide, and polymer chemistry.

In this continuing series of investigations [3–9], the purpose of the present report is to discuss the non-covalent bonding interactions that occur between pyridine and methylpyridine molecules, and the relative position and the possible steric-hindrance effect of the methyl group on the thermodynamic properties of pyridine and methylpyridine aqueous solutions.

Experimental

Materials

Pyridine and methylpyridine isomers (analytical reagents, >99.0%, from Shanghai Chem. Co.) were used without any pretreatment. The water used to prepare solutions was deionized and glass-distilled. The aqueous pyridine and methylpyridine solutions were prepared by mass with a Mettler AE 200 balance with a precision of 0.0001 g.

Methods

The calorimetric system was a 2277-Thermal Activity Monitor produced by Thermometric AB (a company in Stockholm, Sweden) [10]. The 2277-Thermal Activity Monitor is an isothermally thermostated 23 L water bath holding up to four independent calorimetric units and operating at working temperatures between 20 and 80°C. Its stability over 24 h is better than $\pm 10^{-4}$ °C. This monitor is very sensitive, the detection limit is 0.15 μ W and the baseline stability (over a period of 24 h) is 0.20 μ W.

The enthalpies of dilution were measured by a 2277-Thermal Activity Monitor. All measurements were carried out at 298.15 K. Errors in the determinations of the molar enthalpies of dilution were estimated to be <1%. The solutions were pumped through the mixing-flow vessel of the calorimeter using two LKB-2132 microperpex peristaltic pumps. The variation in flow rates was less than 0.1% both before and after a complete dilution experiment. The flow rates were deter-

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mined by weighing the masses of the liquids through each pump within 8 min. The liquids passing through pumps A and B were changed in the following sequence:

- A (water)+B (water), baseline determined
- A (aqueous pyridine or methylpyridine solution)+B (water), dilution thermal power determined
- A (water)+B (water), baseline re-established

The enthalpies of dilution $\Delta_{\text{dil}}H_m$ (J kg^{-1}) were calculated by the equation

$$\Delta_{\text{dil}}H_m = P(1+m_iM)/m_f f_2 \quad (1)$$

where P is the dilution thermal power (μW), m_i is the initial molality of the solution (mol kg^{-1}), M is the molar mass of pyridine or methylpyridine (kg mol^{-1}) and f_2 is the flow rate of pyridine or methylpyridine

Table 1 Enthalpies of dilution of aqueous pyridine and methylpyridine solutions at 298.15 K

$m_i /$	$m_f /$	$\Delta_{\text{dil,exp}}H_m /$	$\Delta_{\text{dil,calc}}H_m /$	$m_i /$	$m_f /$	$\Delta_{\text{dil,exp}}H_m /$	$\Delta_{\text{dil,calc}}H_m /$
mol kg^{-1}		J mol^{-1}		mol kg^{-1}		J mol^{-1}	
Pyridine							
0.1000	0.0493	-71.92 (0.72)	-70.21	0.3200	0.1562	-211.99 (2.12)	-209.53
0.1500	0.0737	-99.22 (0.99)	-101.04	0.3500	0.1707	-232.00 (2.32)	-229.42
0.1800	0.0884	-120.08 (1.21)	-119.74	0.3800	0.1851	-249.38 (2.49)	-249.59
0.2000	0.0981	-129.42 (1.29)	-132.29	0.4000	0.1947	-265.83 (2.66)	-263.19
0.2200	0.1078	-146.16 (1.46)	-144.93	0.4200	0.2043	-269.70 (2.70)	-276.92
0.2500	0.1224	-161.15 (1.61)	-164.06	0.4500	0.2186	-296.03 (2.96)	-297.79
0.2800	0.1369	-185.64 (1.85)	-183.39	0.5000	0.2424	-335.94 (3.36)	-333.30
0.3000	0.1466	-197.32 (1.97)	-196.40				
2-Methylpyridine							
0.1000	0.0492	-9.38 (0.09)	-8.72	0.3000	0.1463	-87.45 (0.87)	-88.85
0.1500	0.0737	-25.50 (0.26)	-26.69	0.3200	0.1559	-95.46 (0.95)	-98.16
0.1800	0.0833	-36.91 (0.37)	-38.09	0.3500	0.1703	-113.41 (1.13)	-112.63
0.2000	0.0980	-48.39 (0.48)	-45.97	0.3800	0.1846	-127.01 (1.27)	-127.71
0.2200	0.1077	-52.06 (0.52)	-54.07	0.4000	0.1942	-137.89 (1.38)	-138.11
0.2500	0.1222	-66.58 (0.67)	-66.66	0.4200	0.2037	-149.49 (1.49)	-148.80
0.2800	0.1367	-84.71 (0.85)	-79.78				
3-Methylpyridine							
0.1000	0.0492	-64.16 (0.6)	-59.04	0.3200	0.1559	-260.43 (2.60)	-260.62
0.1500	0.0737	-99.80 (0.10)	-112.87	0.3500	0.1703	-286.75 (2.87)	-282.91
0.1800	0.0883	-145.40 (1.45)	-142.49	0.3800	0.1846	-307.66 (3.08)	-304.57
0.2000	0.0980	-166.75 (1.67)	-161.24	0.4000	0.1942	-312.65 (3.13)	-318.77
0.2200	0.1077	-178.18 (1.78)	-179.27	0.4200	0.2037	-328.40 (3.28)	-332.84
0.2500	0.1222	-203.67 (2.04)	-205.08	0.4500	0.2179	-355.12 (3.55)	-353.85
0.2800	0.1367	-230.94 (2.31)	-229.60	0.5000	0.2416	-390.85 (3.91)	-389.11
0.3000	0.1463	-246.85 (2.47)	-245.33				
4-Methylpyridine							
0.1000	0.0492	-78.78 (0.79)	-70.96	0.3200	0.1559	-318.50 (3.19)	-316.01
0.1500	0.0737	-116.43 (1.16)	-137.80	0.3500	0.1703	-343.61 (3.44)	-341.88
0.1800	0.0833	-179.76 (1.80)	-174.25	0.3800	0.1846	-375.07 (3.75)	-366.71
0.2000	0.0980	-205.81 (2.06)	-197.17	0.4000	0.1942	-371.50 (3.72)	-382.80
0.2200	0.1077	-218.76 (2.19)	-219.08	0.4200	0.2037	-395.36 (3.95)	-398.62
0.2500	0.1222	-249.55 (2.50)	-250.21	0.4500	0.2179	-422.54 (4.23))	-421.99
0.2800	0.1367	-280.03 (2.80)	-279.47	0.5000	0.2416	-462.96 (4.63))	-460.60
0.3000	0.1463	-296.96 (2.97)	-298.07				

* m_i and m_f are the initial and final molalities of solute. **The values in parentheses are the experimental errors

solution (mg s^{-1}). The final molality m_f was calculated from the equation

$$m_f = m_i f_2 / [f_1 (m_i M_2 + 1) + f_2] \quad (2)$$

where f_1 is the flow rate of water.

Results and discussion

The thermodynamics formalism used to treat the enthalpies of dilution is based on the excess enthalpy concept. The enthalpies of dilution were analysed using a molality expansion of the excess enthalpy. The excess enthalpy per kg of solvent h^E of a binary aqueous solution is defined by [11]

$$h^E = h - h_w^* - mH_2 \quad (3)$$

where h is the enthalpy of a solution of containing 1 kg water and m moles of the solute, h_w^* is the specific enthalpy of water, and H_2 is the partial molar enthalpy of the solute at infinite dilution. The excess enthalpy can be expressed as a power series in the solution molality [12, 13]

$$h^E = h_{xx}m^2 + h_{xxx}m^3 + h_{xxxx}m^4 + \dots \quad (4)$$

where h_{xx} is the enthalpic interaction coefficient which characterizes the interaction between pairs of solvated solute molecules and h_{xxx} , h_{xxxx} contains, at least notionally, contributions from triplet interactions and quartet interactions, respectively. For the dilution of a solution of initial molality m_i to give a solution of final molality m_f , the molar enthalpy of dilution $\Delta_{\text{dil}}H_m$ is given by [13, 14]

$$\Delta_{\text{dil}}H_m = [h^E(m_f)/m_f] - [h^E(m_i)/m_i] \quad (5)$$

where $h^E(m_f)$ is the excess enthalpy for the solution of molality m_f and $h^E(m_i)$ is that for the solution of molality m_i . From Eqs (4) and (5), it follows that

$$\begin{aligned} \Delta_{\text{dil}}H_m = & h_{xx}(m_f - m_i) + \\ & + h_{xxx}(m_f^2 - m_i^2) + h_{xxxx}(m_f^3 - m_i^3) + \dots \end{aligned} \quad (6)$$

or

$$\begin{aligned} \Delta_{\text{dil}}H_m / (m_f - m_i) = & h_{xx} + h_{xxx}(m_f + m_i) + \\ & + h_{xxxx}(m_f^2 + 2m_f m_i + m_i^2) \end{aligned} \quad (7)$$

The experimental values $\Delta_{\text{dil,exp}}H_m$ for solutions of pyridine and methylpyridine, together with the initial and final molalities are given in Table 1. The results were fitted to Eq. (7) using the least-squares procedure. Values of the enthalpic interaction coefficients are given in Table 2. The calculated values $\Delta_{\text{dil,cal}}H_m$ according to Eq. (6) are also listed in Table 1.

As the enthalpic coefficient h_{xxx} contains contributions from multiple interactions and as such is difficult to interpret [12, 15], we will only discuss the h_{xx} coefficients which give a measure of pair associations between solvated solute molecules.

The enthalpic coefficient values of the homogeneous pairs interaction (h_{xx}) reflect the summary process of interaction between two statistical pyridine or methylpyridine molecules in solution proceeding with the participation of water molecules. As can be seen from Table 2, the experimentally observed positive values of h_{xx} indicate that endothermic processes are dominant during the homotactic interaction processes of pyridine and methylpyridine isomers.

To provide a direct interaction between two pyridine and methylpyridine molecules, some water molecules must be removed from the hydration sheaths of the solute molecules since they are a hindrance to their direct contact. The water molecules, pushed out from the hydration sheaths, assume a typical order for 'bulk water'. Thus, the enthalpy coefficients of the homogeneous pairs interaction are a measure of the global effect constituting a sum of the following processes: the partial dehydration of the solutes (an endothermic processes) and the further direct interaction caused by the short-range molecular forces [16, 17]. The direct solute-solute interaction between pyridine or methylpyridine molecules plays the dominant role in the process of interaction. In the processes of the homotactic interactions between molecules, because of the participation of water molecules, pyridine or methylpyridine molecules in aqueous solution can be associated through hydrogen bond (N...H-O) between the nitrogen atom and water molecule. Pyridine acts as a role of 'structure breaker'. Introduction of methyl group into a pyridine molecule may not alter its primary role as the 'structure breaker' to water [1]. The hydrophobic groups in pyridine molecules will stabilize the struc-

Table 2 Homotactic enthalpic interaction coefficients of pyridine and methylpyridine in pure water at 298.15 K

Compounds	$h_{xx} \cdot 10^2 / \text{J kg mol}^{-2}$	$h_{xxx} \cdot 10^2 / \text{J kg}^2 \text{mol}^{-3}$	$h_{xxxx} \cdot 10^2 / \text{J kg}^3 \text{mol}^{-4}$	R^2	SD
Pyridine	11.92	0.17	1.23	0.9987	3.20
2-Methylpyridine	5.98	2.53	1.38	0.9980	2.32
3-Methylpyridine	28.28	-22.64	14.50	0.9974	5.47
4-Methylpyridine	35.77	-29.68	17.73	0.9952	8.78

SD : standard deviation, R^2 : square of relation coefficient

ture of water around them due to 'iceberg formation'. Since the iceberg formation and the destruction of water structure due to the addition of pyridines may tend to cancel, one important factor in this process is the destruction of the self-association which is shown to exist in pyridines from various experimental evidence [18–20].

The direct interaction of pyridine or methylpyridine molecules comprises three kinds of interactions: (a) the hydrophobic-hydrophobic interaction (making positive contributions to h_{xx}); (b) the hydrophobic-hydrophilic interaction (making positive contributions to h_{xx}); (c) the hydrophilic-hydrophilic interaction (making negative contributions to h_{xx}).

In comparison with pyridine, methylpyridine has one hydrophobic group—methyl group. The hydrophobic-hydrophobic interaction between the methyl groups and the hydrophobic-hydrophilic interaction between the methyl group and the nitrogen atom both make positive contributions to h_{xx} coefficients. So to say theoretically, the h_{xx} values of methylpyridine are bigger than that of pyridine. For methylpyridine isomers, the dipole moments of 4-, 3-, 2-methylpyridine are $8.57 \cdot 10^{-30}$ C m, $7.67 \cdot 10^{-30}$ C m, $6.40 \cdot 10^{-30}$ C m, respectively [21]. So their polarities weaken successively and the directive forces decrease in proper order. So relative magnitudes of the interaction forces between molecules are: 4-methylpyridine > 3-methylpyridine > 2-methylpyridine. In addition, the homotactic interaction between molecules will be impaired by the introduction of methyl group at a 2-position, which causes a steric hindrance. Thus in aqueous solutions the relative magnitude of the homotactic interaction coefficients between molecules decrease in the order: $h_{xx}(4\text{-methylpyridine}) > h_{xx}(3\text{-methylpyridine}) > h_{xx}(\text{pyridine}) > h_{xx}(2\text{-methylpyridine})$.

Conclusions

- The homotactic enthalpic pairwise interaction coefficients represent the differences in the total energetic effects of interactions between pyridine or methylpyridine isomers molecules, with the participation of water molecules. The experimentally observed positive values of h_{xx} testify to the predominance of endothermic processes over the effect of exothermic processes.
- The relative magnitudes of h_{xx} values between pyridine or methylpyridine isomers are in the following order: $h_{xx}(4\text{-methylpyridine}) > h_{xx}(3\text{-methylpyridine}) > h_{xx}(\text{pyridine}) > h_{xx}(2\text{-methylpyridine})$, which can be attributed to the introduction and the relative position of methyl group.

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