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# Excess Molar Enthalpies of Binary Mixtures Containing 1-Methyl Pyrrolidin-2-One and Isomeric Picolines

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**ABSTRACT**

Excess molar enthalpies, $H^E$ at the temperature of 298.15 K and atmospheric pressure have been measured for 1-methyl pyrrolin-2-one(i) + α- or β- or γ- picolines (j) binary mixtures over whole range of composition using high sensitivity differential scanning calorimeter Micro DSC (Model – μDSC 7 Evo). The Redlich-Kister equation has been fitted to measure $H^E$ data to estimate binary fitting parameters and standard deviations. The $H^E$ data of 1-methyl pyrrolin-2-one (i) + α- or β- or γ- picolines (j) mixtures are negative across full range of composition. The topology of the constituents of mixtures (Graph theory) has been utilized to predict $H^E$ data.

**KEY WORDS:** Excess molar enthalpy, $H^E$, connectivity parameter of third degree of a molecule, ξ, Interaction energy parameter, χ, picoline.

## 1. INTRODUCTION

The knowledge of thermodynamic properties of liquid mixtures is of substantial significance in chemical industries such as engineering design of separation processes, unit operations and mass transfer (Bhuiyan and Tamura, 2004; Reddy, 2014; Venkatramana, 2014). They are also utilized to test/improve thermodynamic models applied for designing petrochemical processes and heat transfer equipments (Abdulagatov, 2008; Gonzalez, 2008; Saravanan and Maiya, 1998). 1-methyl pyrrolidinone is widely used in industries as co-solvent (to increase the selectivity and solvent power) for the recovery of hydrocarbons from petrochemical processes (Fischer, 1996). Isomeric picolines are n and π electron donor (Saini, 2011). Thus mixtures of 1-methyl pyrrolidinone (as it is recommended for certain pollutant gases separation with organic solvents like picolines) could be used in petroleum industry to enhance recovery of hydrocarbon and also as a way to purify industrial gases stream increasing mass transfer or fluid transfer rate (Domanska and Lachwa 2002). The mass transfer or fluid transfer rate are controlled by thermodynamic properties of liquid mixtures. In continuation of work on thermodynamic properties of liquid mixtures containing lactams as one of the components (Sharma and Rohilla, 2013; Sharma, 2013; Yadav, 2009), excess molar enthalpies data of 1-methyl pyrrolidinone (i) + α- or β- or γ-picoline (j) mixtures are reported at 298.15 K.

## 2. MATERIALS AND METHODS

1-methylpyrrolidin-2-one (NMP) (Fluka 0.99 GC), α-picoline (Fluka, 0.98 GC), β-picoline (Fluka, 0.99 GC) and γ-picoline (Fluka, 0.99 GC) were purified by standard methods (Riddick, 1986). The densities, ρ and speed of sound, u values of the purified liquids measured by using density and sound analyzer apparatus (Dubey and Sharma, 2008) (Anton Paar DSA 5000) at 298.15 ± 0.01 K are presented in table.1, and also compared well with their literature values (Sharma, 2012; Solanki, 2013). The uncertainties in ρ and u are 2 x $10^{-3}$ kg.m$^{-3}$ and $10^{-1}$ m.s$^{-1}$ respectively.

$H^E$ of the studied mixtures were measured by micro differential scanning calorimeter [Model-μ DSC 7 Evo] supplied by M/S SETARAM instrumentation, France in the manner as described elsewhere (Sharma, 2013). The calibration of the calorimeter was done by the joule effect method by measuring heat of fusion of Naphthalene (147.78 J·g$^{-1}$) which in turn is controlled by the SETARAM software.

## 3. RESULTS

The $H^E$ values for NMP (i) + α- or β- or γ-picoline (j) mixtures are presented in table.2, and plotted against mole fraction in figure.1. The $H^E$ were fitted to Redlich-Kister equation

$$H^E = x_i x_j [X^{(0)} + X^{(1)}(2x_i - 1) + X^{(2)}(2x_j - 1)^2] \quad (1)$$

The binary adjustable $H^{(n)}(n = 0 - 2)$ etc. parameters were determined by fitting $H^E$ data to Eq. (1) using least- squares optimization. The binary adjustable parameters of the mixtures along with standard deviations, $\sigma(H^E)$ defined by

$$\sigma(H^E) = [\sum (H^E_{(\exp tl.)} - H^E_{(calc.eq1)})^2 / (m - n)]^{0.5} \quad (2)$$

Where *m* is the number of data points, *n* is the number of adjustable parameters in eq 2 which are reported in table.2.

**Table.1. Comparison of densities, ρ and speeds of sound, u data of pure liquids with their literature values at *T* = 298.15 K**

| Liquids | *T*/K | ρ/kg· m-3 | | u/m·s-1 | |
|---|---|---|---|---|---|
| | | (Expt.) | (Lit.) | (Expt.) | (Lit.) |
| NMP | 298.15 | 1028.26 | 1028.23[15] | 1546.09 | 1546.02[15] |
| α-picoline | 298.15 | 939.807 | 939.802[16] | 1380.17 | 1380.1[16] |
| β-picoline | 298.15 | 952.006 | 952.002[16] | 1424.07 | 1424.0[16] |
| γ-picoline | 298.15 | 950.175 | 950.179[16] | 1431.46 | 1431.5[16] |

The uncertainty in temperature is 0.01 K; The uncertainty in density value ± $10^{-3}$ kg·m$^{-3}$; the uncertainty in speed of sound value is $10^{-1}$ m·s$^{-1}$.

**Table.2. Measured excess molar enthalpies, $H^E$ values for the various (i +j) mixtures as a function of mole fraction xi, of component (i) at T/K = 298.15. Also included are the various $H^{(n)}$(n = 0-2) parameters along with standard deviations σ ($H^E$)**

| $x_i$ | $H^E$ / J. mol-1 | $x_i$ | $H^E$ / J. mol-1 |
|---|---|---|---|
| 1-methylpyrrolidin-2-one (i) + α-picoline (j) | | | |
| 0.0850 | -122.2 | 0.5122 | -411.5 |
| 0.1328 | -182.3 | 0.5796 | -402.6 |
| 0.1913 | -247.0 | 0.6023 | -396.1 |
| 0.2256 | -280.2 | 0.6581 | -372.7 |
| 0.2889 | -332.0 | 0.7159 | -337.1 |
| 0.3358 | -362.3 | 0.7713 | -292.4 |
| 0.3966 | -390.9 | 0.8162 | -248.5 |
| 0.4272 | -400.7 | 0.8788 | -176.2 |
| 0.4537 | -406.7 | 0.9204 | -121.0 |
| $H^{(0)}$ = -1645.8; $H^{(1)}$ = -48.9; $H^{(2)}$ = 50.1; σ($H^E$) = 4 J. mol-1 | | | |
| 1-methylpyrrolidin-2-one (i) + β-picoline (j) | | | |
| 0.0775 | -59.0 | 0.5188 | -250.0 |
| 0.1282 | -96.4 | 0.5705 | -245.2 |
| 0.1750 | -128.9 | 0.6124 | -236.6 |
| 0.2437 | -171.4 | 0.6691 | -218.5 |
| 0.2968 | -199.1 | 0.7238 | -194.3 |
| 0.3321 | -214.5 | 0.7875 | -158.7 |
| 0.3877 | -233.4 | 0.8263 | -133.6 |
| 0.4315 | -243.5 | 0.8728 | -100.6 |
| 0.4723 | -248.8 | 0.9149 | -68.6 |
| $H^{(0)}$ = -1000.7; $H^{(1)}$ = -30.1; $H^{(2)}$ = 209.7; σ( $H^E$) = 2 J. mol-1 | | | |
| 1-methylpyrrolidin-2-one (i) + γ-picoline (j) | | | |
| 0.0919 | -74.7 | 0.5381 | -263.2 |
| 0.1348 | -107.8 | 0.5768 | -258.4 |
| 0.1820 | -141.8 | 0.6324 | -245.2 |
| 0.2239 | -169.4 | 0.6990 | -219.5 |
| 0.2767 | -200.1 | 0.7261 | -206.2 |
| 0.3236 | -222.8 | 0.7780 | -176.4 |
| 0.3754 | -242.5 | 0.8345 | -138.0 |
| 0.4266 | -256.0 | 0.8933 | -92.6 |
| 0.5027 | -264.2 | 0.9141 | -75.4 |
| $H^{(0)}$ = -1056.8; $H^{(1)}$ = -42.3; $H^{(2)}$ =191.1; σ( $H^E$) = 2 J. mol-1 | | | |

The uncertainty in mole fraction value is 1 x 10-4; the uncertainty in temperature is 0.01 K; the uncertainty in $H^E$ values is 1 %.

**Table.3. Comparison of calculated, $H^E$ at T/K = 298.15 values from appropriate equations with their corresponding experimental values and χ*parameters for the various (i + j) mixtures as a function of xi, mole fraction of component (i)**

| Properties | Mole fraction of component | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
| 1-methylpyrrolidin-2-one (i) + α-picoline (j) | | | | | | | | | |
| $H^E$ (Expt.)/J. mol$^{-1}$ | -141.71 | -255.75 | -339.82 | -392.16 | -411.44 | -396.85 | -348.03 | -265.13 | -148.75 |
| $H^E$ (Graph)/J. mol$^{-1}$ | -143.32 | -257.34 | -340.64 | -392.16 | -411.09 | -396.85 | -348.95 | -267.03 | -150.80 |
| $\chi'_{12}$ = -786.75 J. mol$^{-1}$ ; χ* =-1214.03 J. mol$^{-1}$ | | | | | | | | | |
| 1-methylpyrrolidin-2-one (i) + β -picoline (j) | | | | | | | | | |
| $H^E$ (Expt.)/J. mol$^{-1}$ | -75.82 | -145.14 | -200.57 | -236.70 | -250.16 | -239.59 | -205.62 | -150.91 | -80.15 |
| $H^E$ (Graph)/J. mol$^{-1}$ | -86.47 | -155.29 | -205.58 | -236.70 | -248.16 | -239.59 | -210.69 | -161.25 | -91.07 |
| $\chi'_{12}$ = -474.66 J. mol$^{-1}$ ; χ* =-724.18 J. mol$^{-1}$ | | | | | | | | | |
| | | | | | | | | | |
| 1-methylpyrrolidin-2-one (i) + γ-picoline (j) | | | | | | | | | |
| $H^E$ (Expt.)/J. mol$^{-1}$ | -81.05 | -154.01 | -211.94 | -249.76 | -264.19 | -253.82 | -219.05 | -162.13 | -87.15 |
| $H^E$ (Graph)/J. mol$^{-1}$ | -90.40 | -162.94 | -216.37 | -249.76 | -262.41 | -253.82 | -223.57 | -171.34 | -96.89 |
| $\chi'_{12}$ = -493.90 J.mol$^{-1}$ ; χ* = -799.76 J.mol$^{-1}$ | | | | | | | | | |

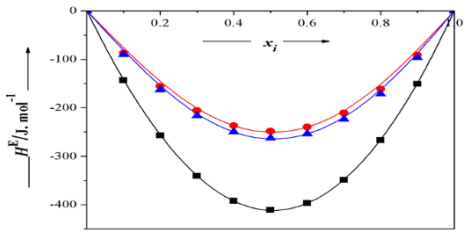


**Figure.1. Experimental excess molar enthalpies, $H^E$ at 298.15 K for (I) 1-methyl pyrrolin-2-one (i) + α-picolines (j). (—■—); (II) 1-methyl pyrrolin-2-one (i) + β-picolines (j); (--●--); (III) 1-methyl pyrrolin-2-one (i) + γ- picolines (j); (--▲--)**

## DISCUSSION

The $H^E$ of NMP (i) + α- or β- or γ-picoline (j) mixtures are not available in the literature to compare experimental data. The $H^E$ data for the investigated mixtures are negative over entire composition range. The $H^E$ data of the (i +j) mixtures is a cumulative effect of contributions, (I) NMP or α- or β- or γ-picoline exist as associated molecular entities; (II) formation of unlike contacts which in turn leads to rupture of associated molecular entities to form their respective monomers; (III) constituent i and j molecules undergo interactions to form i:j molecular complex. The $H^E$ data of the studied mixtures suggest that contribution due to interactions between NMP and α- or β- or γ-picoline far outweigh the contribution due to rupture of associated molecular entities, so that overall $H^E$ values of the mixture are exothermic. The base strength of α- or β- or γ-picoline follow the sequence: α-picoline > β-picoline > γ-picoline which in turn suggest that interactions between NMP and α- or β- or γ-picoline molecule vary in the order γ-picoline > β-picoline > α-picoline. The$H^E$ data for NMP (i) + γ-picoline mixture is less than the NMP + β-picoline mixture may be due to the symmetry of γ-picoline molecule which pack itself more effectively in NMP molecules in comparesion to β-molecule.

**Graph Theory:** The analysis of excess molar volumes, $V^E$ and excess isentropic compressibility's, $\kappa_S^E$ data for NMP (i) + α- or β- or γ-picoline (j) mixtures (Sharma, 2014; Sharma, 2014) in terms of Graph theory and also their spectral data have shown that NMP or α- or β- or γ-picoline exist as associated molecular entities; and are characterized by dipole-dipole interaction. Graph theory was employed to predict $H^E$ data of the NMP (i) + α- or β- or γ-picoline (j) mixtures. For this purpose, it was assumed that investigated (i + j) mixtures formation may involve processes; (1) formation of unlike $i_n$ - $j_n$ contacts; (2) unlike contact formation then weakens $i_n$-$i_n$; jn - jn interactions which leads to the depolymerization of $i_n$, $j_n$ to form i, j monomers; (3) monomers of i and j undergo dipole-dipole interactions to form 1:1 molecular complex. If $\chi_{ij}, \chi_{ii}$ $\chi_{jj}$ and $\chi_{12}$ are interaction parameters for unlike contacts, rupture of associated entities $i_n$, $j_n$ and interactions among the constituents molecules, excess molar enthalpies, then $H^E$ due to

processes (I) – (III) were expressed (Bhagour, 2013; Huggins, 1970, 1971; Neeti, 2011; Sharma and Solanki, 2013; Singh 1983) by

$$H^E=\left[\frac{x_i x_j\left({}^3\xi_i / {}^3\xi_j\right)}{x_i + x_j\left({}^3\xi_i / {}^3\xi_j\right)}\right]\left[\chi_{ij} + x_i\chi_{ii} + x_i\chi_{jj} + x_j\chi_{12}\right] \quad (3)$$

The ${}^3\xi_i (i = i \text{ or } j)$ are the connectivity parameters of third degree, ${}^3\xi$ of the constituent molecules and are defined (Singh, 1986) by

$${}^3\xi = \sum_{m<n<o<p} (\delta_m^v \delta_n^v \delta_o^v \delta_p^v)^{-0.5} \quad (4)$$

Where $\delta_m^v$, etc. values reflects the valency of the atoms forming the bond and have the significance as described elsewhere (Kier, 1980). The ${}^3\xi$ parameters of the constituent molecules in the present mixtures were taken from the literature (Sharma, 2014).

For the present mixtures, it was assumed that energy required to form unlike contacts and rupture of associated molecular entities are nearly equal i.e $\chi_{ij} \cong \chi_{12} = \chi_{12}^{/}$ and $\chi_{ii} \cong \chi_{jj} = \chi^*$ then equation (3) reduced to

$$H^{\mathrm{E}}=\left[\frac{x_i x_j\left({}^3\xi_i / {}^3\xi_j\right)}{x_i + x_j\left({}^3\xi_i / {}^3\xi_j\right)}\right]\left[\left(1+x_j\right)\chi_{12}^{/} + 2x_i\,\chi^*\right] \quad (5)$$

Eq. 5 contain two parameters $\chi_{12}^{/}$, $\chi^*$ and were estimated by using $H^E$ data at two compositions. These parameters were then subsequently utilized to commute $H^E$ values of investigated mixtures at various mole fractions of (i). Such $H^E$ values are recorded in Table 5 and also compared with experimental $H^E$ data. The $\chi_{12}^{/}$, $\chi^*$ parameters along with deviations between experimental $H^E$ values and those obtained from Graph theory are recorded in Table 3. Examination of data in Table 3 suggests that $H^E$ values compare well with their experimental values which in turn support the various assumptions made in deriving Eqs. 5 and also the qualitative analysis of $H^E$ data.

## 4. CONCLUSION

The $H^E$ of NMP (i) + α- or β- or γ-picoline (j) mixtures have been measured across entire composition at 298.15 K and atmospheric pressure. The $H^E$ data for NMP (i) + α- or β- or γ-picoline (j) mixtures for an equimolar composition follow the sequence; β-picoline > γ-picoline > α-picoline; the examination of data in terms of Graph theory suggests that the theoretical values compare reasonably well with the experimental values. The comparison between theoretical $H^E$ estimated by Graph theory and experimental values support the assumptions of various processes involved in the mixtures formation and hence qualitative analysis of measured $H^E$ data.

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**Conflict Of Interest:** The authors declare that there is no conflictof interest regarding the publication of this paper.

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