

## Thermodynamics of molecular interactions in some water + nonelectrolyte mixtures

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Molar excess volumes,  $V^E$ , and molar excess enthalpies,  $H^E$ , for the various water(i) + pyridine or +  $\alpha$ - or +  $\beta$ - or +  $\gamma$ -picoline(j) mixtures have been determined as a function of composition at 298.15 and 308.15 K. The observed data have been analysed by graph theoretical approach which suggest that while water exists as a mixture of dimer and trimer pyridine or  $\alpha$ - or  $\beta$ - or  $\gamma$ -picolines exists as a dimer or an equilibrium mixture of monomer and dimer in pure state. Further these mixtures are characterised predominantly by the presence of 1:1 molecular complex.

Recent studies<sup>1</sup> have shown that water exists as an associated molecular entity in pure state in water + formamide and + N,N-dimethylformamide mixtures. Since pyridine is both N and  $\pi$ -electron donor, the addition of pyridine or its homologues ( $\alpha$ -,  $\beta$ - and  $\gamma$ -picolines) to water may cause (i) rupture of self association in pyridine or its homologues and (ii) structure breaking of water bonding. Thus the addition of pyridine or its homologues to water brings about changes in their respective topology. Since  $V^E$  and  $H^E$  reflects the packing and interactional effects, it would be of interest to extract information about the nature of association in water, pyridine or its homologues from  $V^E$  and  $H^E$  data and the nature of interactions existing between water and nonelectrolyte components.

### Materials and Methods

Pyridine and  $\alpha$ -,  $\beta$ - and  $\gamma$ -picolines (Fluka, A.R. grade) were purified by standard methods<sup>2,3</sup>. Deionised doubly distilled water was used throughout. The purities of the compounds were checked by measuring their densities at  $293.15 \pm 0.01$  K and these agreed to within  $\pm 5 \times 10^{-5}$  g cm<sup>-3</sup> with the corresponding literature values<sup>4-6</sup>.

Molar excess volumes were determined in a V-shaped dilatometer in the manner described elsewhere<sup>7</sup>. The change in the liquid level of the dilatometer capillary was measured with a cathetometer that could read to  $\pm 0.001$  cm. The uncertainty in our measured  $V^E$  values is  $\pm 0.5\%$ .

Molar excess enthalpies for the various mixtures were measured in a flow microcalorimeter (LKB Broma, Sweden) in the manner described elsewhere<sup>8</sup>. The uncertainty in the measured  $H^E$  values is  $\sim 1\%$ .

### Results

Molar excess volumes,  $V^E$ , and molar excess enthalpies for the various (i+j) mixtures as a function of composition at 298.15 and 308.15 K, recorded in Tables 1 and 2, can be expressed as

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

where  $x_i$  is the mole fraction of component i.  $X^n$  ( $n=0-2$ ) are adjustable parameters. These parameters were obtained by fitting  $X^E$  ( $X=V$  or  $H$ )/ $x_i(1-x_i)$  data to Eq. 1 by the method of least squares. These parameters are recorded together with the standard deviations  $\sigma(X^E)$  of  $X$  ( $X=V$  or  $H$ ) defined by

$$\sigma(X^E) = [\sum (X_{\text{Exptl}}^E - X_{\text{Calc. Eq. 1}}^E)^2 / (m-p)]^{0.5} \quad \dots (2)$$

(where  $X_{\text{Exptl}}^E$  is the experimentally measured values and  $X_{\text{Calc. Eq. 1}}^E$  is the values calculated from Eq. 1,  $m$  is the number of data points and  $p$  is the number of adjustable parameters in Eq. 1) in Tables 1 and 2.

### Discussion

We are unaware of any  $V^E$  and  $H^E$  data for the water (i) + pyridine, +  $\alpha$ -, +  $\beta$ - and +  $\gamma$ -picoline (j) mixtures with which to compare our results.  $V^E$  and  $H^E$  values for the (i+j) mixtures are ne-

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Table 1—Measured  $V^E$  values at 298.15 and 308.15 K for the various (i+j) mixtures as functions of  $x_i$ , the mole fraction of component i; also included are the various  $V^{(n)}$  ( $n=0-2$ ) parameters alongwith standard deviation  $\sigma(V^E)$ 

$x_i$	$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	$x_i$	$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	$x_i$	$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	$x_i$	$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )
Water (i) + pyridine (j)				Water (i) + $\beta$ -picoline (j)			
At 298.15 K				At 298.15 K			
0.0811	-0.102	0.6790	-0.579	0.0861	-0.149	0.5120	-0.748
0.1461	-0.198	0.7211	-0.538	0.1290	-0.232	0.5981	-0.728
0.2793	-0.398	0.8162	-0.409	0.2130	-0.398	0.6821	-0.648
0.3462	-0.481	0.8961	-0.255	0.2831	-0.530	0.7922	-0.461
0.4182	-0.555	0.9221	-0.199	0.3340	-0.607	0.8103	-0.432
0.5283	-0.617	0.9721	-0.078	0.4080	-0.693	0.9012	-0.232
0.5970	-0.618			0.4675	-0.736	0.9720	-0.065
$V^{(0)} = -2.421$ ; $V^{(1)} = -0.819$ ; $V^{(2)} = 0.494$ ; $\sigma(V^E) = 0.005$				$V^{(0)} = -2.984$ ; $V^{(1)} = -0.408$ ; $V^{(2)} = 1.120$ ; $\sigma(V^E) = 0.004$			
At 308.15 K				At 308.15 K			
0.0691	-0.079	0.6190	-0.570	0.0751	-0.115	0.5211	-0.664
0.1520	-0.195	0.6981	-0.525	0.1230	-0.200	0.5822	-0.642
0.2461	-0.128	0.7643	-0.452	0.1723	-0.289	0.6282	-0.608
0.3282	-0.440	0.8452	-0.324	0.2310	-0.394	0.7193	-0.494
0.4160	-0.528	0.9020	-0.219	0.2931	-0.495	0.8012	-0.357
0.4981	-0.571	0.9681	-0.074	0.3412	-0.560	0.8923	-0.187
0.5463	-0.585			0.4763	-0.661	0.9568	-0.069
$V^{(0)} = -2.297$ ; $V^{(1)} = -0.703$ ; $V^{(2)} = 0.637$ ; $\sigma(V^E) = 0.006$				$V^{(0)} = -2.657$ ; $V^{(1)} = -0.101$ ; $V^{(2)} = 1.310$ ; $\sigma(V^E) = 0.004$			
Water (i) + $\alpha$ -picoline (j)				Water (i) + $\gamma$ -picoline (j)			
At 298.15 K				At 298.15 K			
0.0582	-0.155	0.5874	-1.008	0.0851	-0.155	0.5921	-0.837
0.1386	-0.358	0.6672	-0.964	0.1312	-0.256	0.6480	-0.782
0.2181	-0.545	0.7280	-0.886	0.2180	-0.456	0.7141	-0.680
0.2993	-0.714	0.7985	-0.745	0.3012	-0.633	0.7853	-0.532
0.3685	-0.844	0.8653	-0.555	0.3853	-0.770	0.8431	-0.397
0.4267	-0.922	0.9128	-0.386	0.4431	-0.833	0.9421	-0.149
0.5091	-0.992	0.9682	-0.153	0.5212	-0.804	0.9773	-0.050
$V^{(0)} = -3.949$ ; $V^{(1)} = -1.230$ ; $V^{(2)} = 0.152$ ; $\sigma(V^E) = 0.005$				$V^{(0)} = -3.443$ ; $V^{(1)} = -0.449$ ; $V^{(2)} = 1.618$ ; $\sigma(V^E) = 0.004$			
At 308.15 K				At 308.15 K			
0.0658	-0.149	0.5981	-0.994	0.0621	-0.075	0.6020	-0.792
0.1253	-0.294	0.6852	-0.916	0.1243	-0.187	0.7240	-0.622
0.3287	-0.764	0.7683	-0.764	0.2013	-0.357	0.7921	-0.477
0.4162	-0.907	0.8265	-0.620	0.2952	-0.564	0.8520	-0.330
0.4891	-0.978	0.8951	-0.405	0.3741	-0.706	0.9322	-0.142
0.5462	-0.996	0.9656	-0.143	0.4321	-0.780	0.9710	-0.055
$V^{(0)} = -3.934$ ; $V^{(1)} = -1.103$ ; $V^{(2)} = 0.768$ ; $\sigma(V^E) = 0.005$				$V^{(0)} = -3.279$ ; $V^{(1)} = -0.534$ ; $V^{(2)} = 2.057$ ; $\sigma(V^E) = 0.004$			
				$V^{(n)}$ ( $n=0-2$ ) and $\sigma(V^E)$ are in cm <sup>3</sup> mol <sup>-1</sup>			

Table 2—Measured  $H^E$  values at 298.15 and 308.15 K for the various (i+j) mixtures as functions of  $x_i$ , the mole fraction of component i; also included are the various  $H^{(n)}$  ( $n=0-2$ ) parameters alongwith standard deviation  $\sigma(H^E)$

$x_i$	$H^E$ (J mol <sup>-1</sup> )	$x_i$	$H^E$ (J mol <sup>-1</sup> )	$x_i$	$H^E$ (J mol <sup>-1</sup> )	$x_i$	$H^E$ (J mol <sup>-1</sup> )
Water (i) + pyridine (j)				Water (i) + $\beta$ -picoline (j)			
At 298.15 K				At 298.15 K			
0.0499	-141.6	0.5021	-1035.4	0.0387	-95.3	0.5024	-1049.8
0.0847	-237.8	0.5582	-1059.4	0.0859	-213.8	0.5862	-1022.4
0.1556	-412.3	0.6585	-1032.0	0.1623	-434.3	0.6483	-956.3
0.1898	-508.4	0.7505	-889.1	0.2487	-679.8	0.7089	-847.4
0.2886	-728.2	0.7918	-818.6	0.2980	-790.0	0.7861	-660.0
0.3254	-800.9	0.8604	-609.3	0.3553	-910.3	0.8486	-480.3
0.3902	-916.7	0.9216	-389.6	0.3907	-956.8	0.9070	-285.1
0.4501	-979.1	0.9701	-164.3	0.4675	-1035.3	0.9607	-112.8
$H^{(0)} = -4133.89$ ; $H^{(1)} = -1391.88$ ; $H^{(2)} = -8.92$ ; $\sigma(H^E) = 6.31$				$H^{(0)} = -4202.71$ ; $H^{(1)} = -370.3$ ; $H^{(2)} = 1602.91$ ; $\sigma(H^E) = 5.21$			
At 308.15 K				At 308.15 K			
0.0507	-210.1	0.6195	-990.0	0.0438	-72.1	0.4999	-874.5
0.0817	-326.7	0.6705	-926.8	0.0926	-182.3	0.5628	-870.6
0.1499	-539.9	0.7313	-808.1	0.1784	-371.6	0.6091	-838.8
0.2011	-680.8	0.7789	-700.3	0.2487	-539.5	0.6972	-730.3
0.2717	-895.2	0.5489	-538.8	0.2983	-634.6	0.7686	-605.5
0.3486	-980.3	0.8927	-380.3	0.3477	-732.3	0.8020	-524.7
0.4905	-1069.9	0.9514	-192.6	0.3982	-806.2	0.9350	-182.9
0.5898	-1010.0	0.9706	-120.8	0.4674	-859.4	0.9785	-50.8
$H^{(0)} = -4245.04$ ; $H^{(1)} = 152.13$ ; $H^{(2)} = 145.76$ ; $\sigma(H^E) = 7.82$				$H^{(0)} = -3503.96$ ; $H^{(1)} = -520.49$ ; $H^{(2)} = 1461.51$ ; $\sigma(H^E) = 5.49$			
Water (i) + $\alpha$ -picoline (j)				Water (i) + $\gamma$ -picoline (j)			
At 298.15 K				At 298.15 K			
0.0528	-165.3	0.5087	-1288.6	0.0487	-135.2	0.5349	-920.8
0.0984	-309.4	0.5767	-1284.1	0.1210	-340.3	0.5824	-898.0
0.1562	-497.3	0.6501	-1225.4	0.2208	-592.5	0.6225	-863.1
0.1909	-620.8	0.7108	-1108.1	0.3191	-782.2	0.7311	-698.2
0.2464	-799.7	0.7982	-850.3	0.3603	-842.4	0.7824	-585.0
0.3012	-948.9	0.8475	-679.4	0.4059	-886.6	0.8126	-512.2
0.3878	-1156.3	0.8987	-460.9	0.4382	-913.2	0.8904	-308.6
0.4651	-1267.5	0.9562	-202.6	0.4865	-927.1	0.9461	-154.8
$H^{(0)} = -5151.94$ ; $H^{(1)} = -1050.44$ ; $H^{(2)} = 1327.81$ ; $\sigma(H^E) = 6.07$				$H^{(0)} = -3716.88$ ; $H^{(1)} = -16.85$ ; $H^{(2)} = 845.56$ ; $\sigma(H^E) = 6.71$			
At 308.15 K				At 308.15 K			
0.0382	-132.7	0.4950	-1321.3	0.0586	-175.3	0.5875	-825.3
0.0849	-308.6	0.5885	-1317.6	0.1087	-300.2	0.6462	-784.3
0.1462	-539.3	0.6404	-1250.5	0.1934	-566.2	0.7137	-682.6
0.1903	-692.4	0.7082	-1139.1	0.2671	-656.1	0.7859	-563.7
0.2684	-934.3	0.7642	-990.4	0.3084	-707.6	0.8462	-420.4
0.3001	-1024.8	0.8282	-778.3	0.3842	-807.8	0.8962	-306.8
0.3784	-1184.5	0.9206	-396.4	0.4697	-845.3	0.9240	-218.3
0.4409	-1278.5	0.9785	-118.7	0.5062	-853.2	0.9604	-110.3
$H^{(0)} = -5304.35$ ; $H^{(1)} = -803.94$ ; $H^{(2)} = 905.65$ ; $\sigma(H^E) = 5.94$				$H^{(0)} = -3421.30$ ; $H^{(1)} = -47.06$ ; $H^{(2)} = 392.01$ ; $\sigma(H^E) = 6.52$ $H^{(n)}$ ( $n=0-2$ ) and $(H^E)$ are in J mol <sup>-1</sup>			

gative over the entire range of composition at 298.15 and 308.15 K. While  $V^E$  data for equimolar composition at 308.15 K vary in the order pyridine >  $\beta$ -picoline >  $\gamma$ -picoline >  $\alpha$ -picoline,  $H^E$  data for equimolar mixture vary in the order  $\gamma$ -picoline >  $\beta$ -picoline > pyridine >  $\alpha$ -picoline.

At the simplest qualitative level, the present  $H^E$  data for the various (i+j) mixtures may be explained on the basis of the following assumptions:

(i) water, pyridine,  $\alpha$ -,  $\beta$ - and  $\gamma$ -picolines are associated entities in pure state; (ii) pyridine,  $\alpha$ -,  $\beta$ - and  $\gamma$ -picoline undergo specific interactions with water; (iii) specific interaction between water and pyridine,  $\alpha$ -,  $\beta$ - and  $\gamma$ -picoline weakens the i-i or j-j interactions resulting in their depolymerization; and (iv) the respective monomers then undergo specific interaction to form i-j molecular entity.

$H^E$  data for water(i) + pyridine(j) mixtures suggest that contribution to observed  $H^E$  data due to unlike interactions [due to factor (ii) and (iv)] outweigh those due to like interactions [due to factor (iii)]. Since the base strengths of pyridine and  $\alpha$ -,  $\beta$ - and  $\gamma$ -picolines increases<sup>9</sup> in the order, pyridine <  $\gamma$ -picoline <  $\beta$ -picoline <  $\alpha$ -picoline, it would then mean that interactions between  $\pi$ -electron cloud on N-atom in picolines and hydrogen atom of water must be stronger in water +  $\alpha$ -picoline mixture than water +  $\beta$ -picoline or water +  $\gamma$ -picoline mixtures and should vary in the order  $\gamma$ -picoline >  $\beta$ -picoline >  $\alpha$ -picoline.

The experimental  $H^E$  values for these mixtures support this view point. However more negative  $H^E$  values for water(i) + pyridine(j) mixtures than water(i) +  $\beta$ - and +  $\gamma$ -picoline(j) mixtures suggest that contribution to observed  $H^E$  due to factors (ii) and (iv) is more predominant in water(i) + pyridine(j) mixtures. The  $V^E$  values suggest that pyridine gives least packed arrangement while picolines give relatively more packed structure.

If the addition of water(i) to pyridine,  $\alpha$ -,  $\beta$ - and  $\gamma$ -picoline(j) causes changes in the topology of i and or j, it must be reflected in the equilibrium thermodynamic properties of the (i+j) mixture. Since  $V^E$  is a packing effect, it would be worthwhile to analyse  $V^E$  data in terms of graph-theoretical approach<sup>10,11</sup> that employs connectivity parameter of the third degree. With assumption of no particular molecular state for i and j,  $V^E$  according to this approach is given by Eq. 3,

$$V^E = \alpha_{ij} [\sum \{x_i ({}^3\xi_i)_m\}^{-1} - \sum x_i / {}^3\xi_i] \quad \dots (3)$$

where  ${}^3\xi_i$  and  $({}^3\xi_i)_m$  in Eq. 3 denote respectively the connectivity parameter to the third degree of

component i in the pure state and in the mixture and is defined<sup>12</sup> by

$${}^3\xi = \sum_{m < n < o < p} [\delta_m^v \delta_n^v \delta_o^v \delta_p^v]^{-1/2} \quad \dots (4)$$

where  $\delta_m^v$  etc. have the same significance as described elsewhere<sup>12</sup>. Again as the degree of association of i and j is not known with certainty,  $({}^3\xi_i)_m$  and  ${}^3\xi_i$  (i=i or j) are regarded as adjustable parameters and evaluated by fitting  $V^E$  data to Eq. 3. Only those  $({}^3\xi_i)_m$  and  ${}^3\xi_i$  (i=i or j) values were retained that best reproduced the experimental data i.e. for which the variance to fit,  $\rho$ , defined by  $\rho = \sum [V_{\text{exptl.}} - V_{\text{calc.}}]^2 / (Q-P)^{0.5}$ , (where (Q-P) is the number of degrees of freedom) was minimum. Such  $({}^3\xi_i)_m$  and  ${}^3\xi_i$  etc. values along with  $V^E$  values (calculated using Eq. 3) at various  $x_i$  are recorded in Table 3.

A number of structures were then assumed for water, pyridine and  $\alpha$ -,  $\beta$ - and  $\gamma$ -picolines, and their  ${}^3\xi'$  values were determined from structural considerations. These  ${}^3\xi'$  values were then compared with the corresponding  ${}^3\xi$  values obtained for them via Eq. 3 from  $V^E$  data. Any structure or combination of structures that yielded a  ${}^3\xi'$  value that compared well with  ${}^3\xi$  values (calculated via Eq. 4) was taken to be a good representation of the structure of that component.

For the present (i+j) mixtures, it was assumed that water(i) exists as molecular entities I-VI. The  ${}^3\xi'$  values for these molecular entities were then calculated to be 0.426, 1.379, 1.462, 1.229, 1.328 and 1.072 respectively. Since water was found to have  ${}^3\xi$  value of 1.05 in water(i) +  $\beta$ -picoline mixture, the present analysis suggests that water in pure state exists as an equilibrium mixture of I, IV and V (average  ${}^3\xi' = 1.088$ ) or an equilibrium mixture of I, II and IV (average  ${}^3\xi' = 1.229$ ). This observation is consistent with the more involved studies<sup>1,13,14</sup> on the state of aggregation of liquid water. Further,  ${}^3\xi'$  values of 0.601, 0.602 and 0.603 for water in water(i) + pyridine, +  $\alpha$ - and +  $\gamma$ -picoline(j) mixtures suggest the presence of a mixture of molecular entities I and VI (average  ${}^3\xi' = 0.749$ ). *Ab initio* molecular orbital calculation<sup>15</sup> on the structural energetic and electronic properties of  $\beta$ - and  $\gamma$ -R-pyridines (R = CH<sub>3</sub>, NH<sub>2</sub>, OH, F etc.) have suggested that  $\pi$ -electron cloud density at C<sub>2</sub>, C<sub>4</sub> and C<sub>6</sub> positions in pyridine is less than that in benzene. This suggests that either one, two or all three electron-deficient carbon atoms in pyridine or its homologues ( $\alpha$ -,  $\beta$ - and  $\gamma$ -picolines) are involved in weak interactions with the  $\pi$ -electron cloud of other molecule. Consequently, it was assumed that for the present

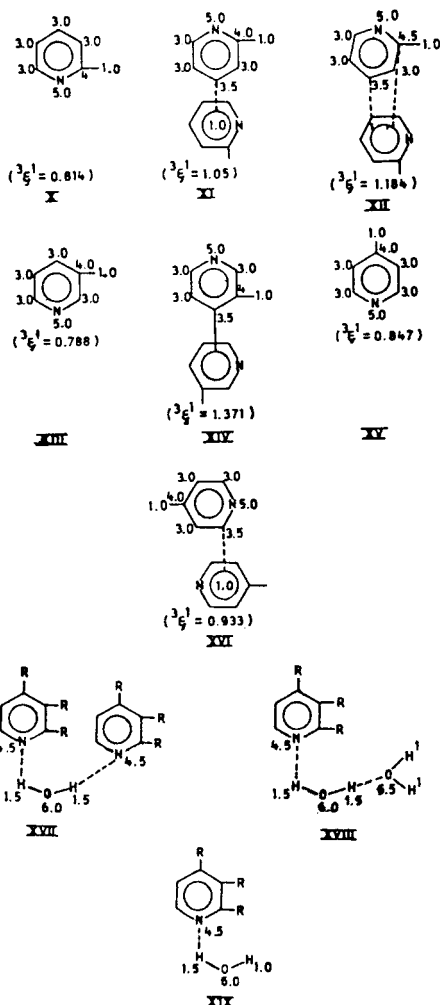
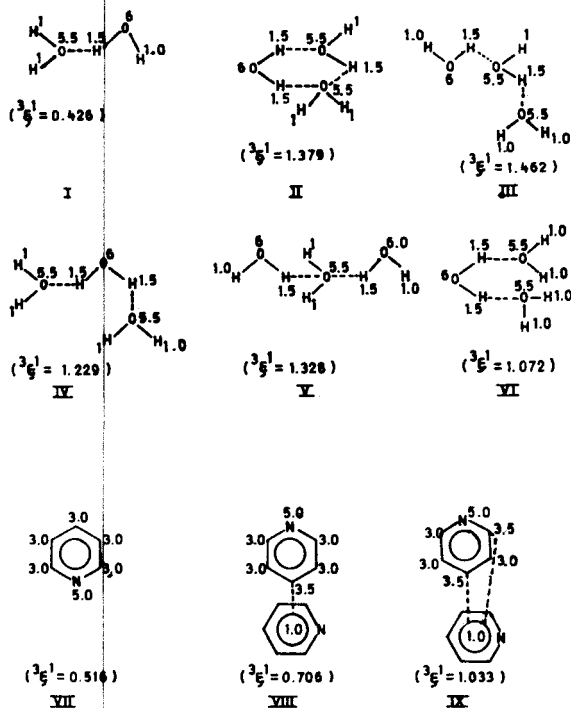
mixtures pyridine and  $\alpha$ -,  $\beta$ - and  $\gamma$ -picolines exist as VII-IX, X-XII, XIII-XIV, XV-XVI molecular entities. It was assumed that in molecular entities IX and XII electron deficient centres  $C_2$  and  $C_4$  are involved in weak interactions with the  $\pi$ -electron cloud of pyridine ring. The  $\delta^v$  value for the various vertices are shown in molecular entities. It was, however, assumed that in molecular entities VIII, IX, XI, XII, XIV, XV,  $\delta^v(\pi=1)^{10}$  (where  $\pi$ -electron cloud of one molecule is involved in specific interaction with another molecule).

The  ${}^3\xi_j^i$  values for the entities VII to XVI were then calculated to be 0.516, 0.706, 1.033, 0.814, 1.05, 1.184, 0.788, 1.371, 0.847 and 0.933 respectively.  ${}^3\xi_j^i$  values of 1.30, 1.20, 0.80 and 0.85 for pyridine,  $\alpha$ -,  $\beta$ - and  $\gamma$ -picolines (Table 3) in the present (i+j) mixtures suggest that pyridine and  $\alpha$ -picoline exist as dimers (mixture of molecular entities VIII-IX and XI-XII respectively). On the other hand  $\beta$ - and  $\gamma$ -picolines exist as equilibrium mixtures of monomer and dimer.

Further, in the present (i+j) mixtures, if it was assumed that nitrogen atom attached to pyridine or its homologues ring is involved in hydrogen bonding with the hydrogen atom of water molecule, then the molecular entity that should determine  $({}^3\xi_j^i)_m$  value of j in these mixtures should be XVII, XVIII or XIX with R = H or  $CH_3$ . Postulating molecular entity XVII in these mixtures would then yield  $({}^3\xi_j^i)_m$  values of 1.930, 2.438, 2.144 and 2.132 for pyridine and  $\alpha$ -,  $\beta$ - and  $\gamma$ -picolines re-

spectively. On the other hand  $({}^3\xi_j^i)_m$  values for pyridine and  $\alpha$ -,  $\beta$ - and  $\gamma$ -picolines would be 1.491, 1.730, 1.476 and 1.450 for molecular entity XVIII and 1.089, 1.459, 1.181 and 1.134 for molecular entity XIX. It is thus evident that only  $({}^3\xi_j^i)_m$  values evaluated for pyridine and  $\alpha$ -,  $\beta$ - and  $\gamma$ -picolines (j) are very close to the corresponding  $({}^3\xi_j^i)_m$  values of 1.30, 1.20, 0.80 and 0.85 (Table 3) for molecular entity XIX. The present analysis thus suggests that pyridine and  $\alpha$ -,  $\beta$ - and  $\gamma$ -picolines are associated entities and that all these mixtures are characterised predominantly by the presence of molecular entity XIX which lends additional support to the qualitative discussion of  $H^E$  data for these mixtures.

In order to understand the energetics of various interactions that characterize these mixtures, it was assumed that mixture formation involves (a) the establishment of unlike contact between i and j (b) the establishment of unlike contact formation between i and j then influences i-i and j-j interactions that ultimately yields respective monomers and (c) the respective monomers then undergo



specific interactions to give i-j molecular entity. Consequently, if  $\alpha_{ij}$  is the molar enthalpy interaction parameter of i-j contact formation, then change in enthalpy due to process (a) would be given<sup>16,17</sup> by

$$\Delta H_1 = x_i \alpha_{ij} S_j \quad \dots (5)$$

where  $S_j$  is the surface fraction of j involved in i-j contact and is defined<sup>18,19</sup> by

$$S_j = x_j V_j / \sum x_i V_i \quad \dots (6)$$

so that

$$\Delta H_1 = x_i x_j \alpha_{ij} V_j / \sum x_i V_i \quad \dots (7)$$

Further if  $\alpha_{ii}$  and  $\alpha_{jj}$  are the molar interaction energies for i-i and j-j contact, then enthalpy change due to process(b) would be given<sup>20</sup> by

$$\Delta H_2 = k \alpha_{ii} x_i^2 x_j V_j / \sum x_i V_i \quad \dots (8)$$

$$\Delta H_3 = k' \alpha_{jj} x_i^2 x_j V_j / \sum x_i V_i \quad \dots (9)$$

where  $k$  and  $k'$  are constants.

The enthalpy changes due to process (c) would, however, be given<sup>20</sup> by

$$\Delta H_4 = k'' x_i^2 x_j \alpha_{12} V_j / \sum x_i V_i \quad \dots (10)$$

where  $\alpha_{12}$  is the interaction energy per mole for process(c) resulting in the formation of i-j molecular entities and  $k''$  is a constant of proportionality. The overall enthalpy change due to processes(a)-(c) would then be given by

$$H^E = \sum_{i=1}^4 \Delta H_i = [x_i x_j V_j / \sum x_i V_i] [\alpha_{ij} + k \alpha_{ii} x_i + k' \alpha_{jj} x_i + k'' \alpha_{12} x_j] \quad \dots (11)$$

Table 3—Comparison of  $V^E$  and  $H^E$  values (calculated from appropriate equations (see text) with the corresponding experimental values at 298.15 and 308.15 K for the various (i + j) mixtures as functions of  $x_i$ , mole fraction of i; also included are the various interaction energies  $X_i$ ,  $X'$  parameters

Property	$x_i$							
	0.1	0.2	0.3	0.4	0.6	0.7	0.8	0.9
Water (i) + pyridine (j)								
At 298.15 K								
$V_{(expt)}^E$	-0.139	-0.281	-0.424	-0.538	-0.615	-0.559	-0.436	-0.246
$V_{(calc)}^E$	-0.165	-0.312	-0.435	-0.532	-0.616	-0.586	-0.487	-0.304
$H_{(expt)}^E$	-275.0	-530.7	-753.5	—	-1058.8	-984.1	-793.1	-468.8
$H_{(calc)}^E$	-240.1	-504.2	-738.9	—	-1049.2	-961.8	-718.5	-434.8
${}^3\xi_i = ({}^3\xi_i)_m = 0.601$ ; ${}^3\xi_j = ({}^3\xi_j)_m = 1.30$ ; $\alpha_{ij} = 3.599 \text{ cm}^3 \text{ mol}^{-1}$ ; $X_i = -1056.5 \text{ J mol}^{-1}$ ; $X' = -4972.7 \text{ J mol}^{-1}$								
At 308.15 K								
$V_{(expt)}^E$	-0.120	-0.264	-0.403	-0.503	-0.588	-0.519	-0.396	-0.218
$V_{(calc)}^E$	-0.160	-0.302	-0.423	-0.516	-0.598	-0.569	-0.474	-0.268
$H_{(expt)}^E$	-388.0	-687.1	-901.2	—	-1009.1	-872.0	-653.2	-360.1
$H_{(calc)}^E$	-393.3	-695.7	-900.1	—	-1012.4	-880.9	-629.9	-366.2
${}^3\xi_i = ({}^3\xi_i)_m = 0.601$ ; ${}^3\xi_j = ({}^3\xi_j)_m = 1.30$ ; $\alpha_{ij} = 3.497 \text{ cm}^3 \text{ mol}^{-1}$ ; $X_i = -2232.1 \text{ J mol}^{-1}$ ; $X' = -3379.7 \text{ J mol}^{-1}$								
Water (i) + $\alpha$ -picoline (j)								
At 298.15 K								
$V_{(expt)}^E$	-0.261	-0.507	-0.723	-0.888	-1.005	-0.926	-0.738	-0.431
$V_{(calc)}^E$	-0.280	-0.527	-0.732	-0.889	-1.016	-0.957	-0.789	-0.484
$H_{(expt)}^E$	-314.9	-650.2	-951.7	—	-1273.1	-1123.3	-845.3	-458.5
$H_{(calc)}^E$	-345.3	-679.6	-965.5	—	-1290.7	-1171.1	-919.5	-531.0
${}^3\xi_i = ({}^3\xi_i)_m = 0.602$ ; ${}^3\xi_j = ({}^3\xi_j)_m = 1.20$ ; $\alpha_{ij} = 7.196 \text{ cm}^3 \text{ mol}^{-1}$ ; $X_i = -1677.2 \text{ J mol}^{-1}$ ; $X' = -5199.7 \text{ J mol}^{-1}$								
At 308.15 K								
$V_{(expt)}^E$	-0.233	-0.481	-0.709	-0.885	-0.989	-0.891	-0.688	-0.385
$V_{(calc)}^E$	-0.279	-0.525	-0.729	-0.885	-1.011	-0.953	-0.786	-0.482
$H_{(expt)}^E$	-371.0	-722.6	-1018.1	—	-1302.2	-1148.8	-870.3	-478.7
$H_{(calc)}^E$	-389.2	-740.9	-1027.3	—	-1313.2	-1180.7	-919.0	-423.5
${}^3\xi_i = ({}^3\xi_i)_m = 0.602$ ; ${}^3\xi_j = ({}^3\xi_j)_m = 1.20$ ; $\alpha_{ij} = 7.167 \text{ cm}^3 \text{ mol}^{-1}$ ; $X_i = -1984.8 \text{ J mol}^{-1}$ ; $X' = -4965.3 \text{ J mol}^{-1}$								

(—Contd)

Table 3—Comparison of  $V^E$  and  $H^E$  values (calculated from appropriate equations (see text) with the corresponding experimental values at 298.15 and 308.15 K for the various (i+j) mixtures as functions of  $x_i$ , mole fraction of i; also included are the various interaction energies  $X_i$ ,  $X'$  parameters—Contd

Property	$x_i$							
	0.1	0.2	0.3	0.4	0.6	0.7	0.8	0.9
Water (i) + $\beta$ -picoline (j)								
At 298.15 K								
$V_{\text{exptl}}^E$	-0.176	-0.376	-0.554	-0.684	-0.724	-0.622	-0.450	-0.231
$V_{\text{calc}}^E$	-0.296	-0.519	-0.662	-0.735	-0.697	-0.594	-0.441	-0.222
$H_{\text{exptl}}^E$	-262.0	-547.3	-799.9	—	-1010.0	-857.7	-612.8	-309.4
$H_{\text{calc}}^E$	-333.4	-611.6	-827.9	—	-1042.9	-940.6	-744.3	-433.7
${}^3\xi_i = ({}^3\xi_i)_m = 1.05$ ; ${}^3\xi_j = ({}^3\xi_j)_m = 0.80$ ; $\alpha_{ij} = 37.096 \text{ cm}^3 \text{ mol}^{-1}$ ; $X_i = -1799.4 \text{ J mol}^{-1}$ ; $X' = -1004.8 \text{ J mol}^{-1}$								
At 308.15 K								
$V_{\text{exptl}}^E$	-0.158	-0.342	-0.507	-0.620	-0.631	-0.521	-0.350	-0.171
$V_{\text{calc}}^E$	-0.264	-0.464	-0.589	-0.655	-0.620	-0.529	-0.392	-0.215
$H_{\text{exptl}}^E$	-195.9	-428.8	-644.9	—	-851.2	-728.7	-524.0	-265.9
$H_{\text{calc}}^E$	-262.3	-488.5	-671.0	—	-883.5	-805.7	-645.9	-381.2
${}^3\xi_i = ({}^3\xi_i)_m = 1.05$ ; ${}^3\xi_j = ({}^3\xi_j)_m = 0.80$ ; $\alpha_{ij} = 33.018 \text{ cm}^3 \text{ mol}^{-1}$ ; $X_i = -1393.8 \text{ J mol}^{-1}$ ; $X' = -997.8 \text{ J mol}^{-1}$								
Water (i) + $\gamma$ -picoline (j)								
At 298.15 K								
$V_{\text{exptl}}^E$	-0.184	-0.414	-0.631	-0.789	-0.707	-0.605	-0.501	-0.243
$V_{\text{calc}}^E$	-0.263	-0.482	-0.653	-0.773	-0.827	-0.751	-0.593	-0.346
$H_{\text{exptl}}^E$	-287.3	-546.7	-752.4	—	-883.2	-751.8	-545.2	-284.2
$H_{\text{calc}}^E$	-321.7	-578.2	-766.6	—	-899.5	-792.5	-609.0	-344.2
${}^3\xi_i = ({}^3\xi_i)_m = 0.603$ ; ${}^3\xi_j = ({}^3\xi_j)_m = 0.85$ ; $\alpha_{ij} = 19.928 \text{ cm}^3 \text{ mol}^{-1}$ ; $X_i = -1766.0 \text{ J mol}^{-1}$ ; $X' = -1839.8 \text{ J mol}^{-1}$								
At 308.15 K								
$V_{\text{exptl}}^E$	-0.142	-0.337	-0.574	-0.743	-0.793	-0.662	-0.450	-0.213
$V_{\text{calc}}^E$	-0.258	-0.474	-0.643	-0.761	-0.814	-0.739	-0.581	-0.341
$H_{\text{exptl}}^E$	-284.5	-522.4	-702.8	—	-818.8	-707.7	-527.2	-286.1
$H_{\text{calc}}^E$	-299.6	-536.7	-709.4	—	-826.0	-724.4	-556.9	-314.1
${}^3\xi_i = ({}^3\xi_i)_m = 0.603$ ; ${}^3\xi_j = ({}^3\xi_j)_m = 0.85$ ; $\alpha_{ij} = 19.617 \text{ cm}^3 \text{ mol}^{-1}$ ; $X_i = -1651.2 \text{ J mol}^{-1}$ ; $X' = -1655.1 \text{ J mol}^{-1}$								

Since  $V_j/V_i$  has been equal to  ${}^3\xi_i/{}^3\xi_j = (Y)$ , then Eq. 11 reduces to

$$H^E = [x_i x_j Y / (x_i + x_j Y)] [x_{ij} + k x_i x_{ii} + k' x_i x_{jj} + k'' x_j x_{12}] \dots (12)$$

For the present (i+j) mixtures, it would, however, be more reasonable to assume that

$$x_{ij} \approx k x_{12} \approx X_i$$

and

$$k' x_{ii} \approx k'' x_{jj} = X'$$

so that Eq. 12 reduces to

$$H^E = [x_i x_j Y / (x_i + x_j Y)] [(1 + x_j) X_i + 2x_i X'] \dots (13)$$

Equation 13 contains two unknown parameters ( $X_i$  and  $X'$ ) and for the present analysis, we em-

ployed  $H^E$  data at arbitrary compositions ( $x_i = 0.4$  and  $0.5$ ) to evaluate them using Eq. 13. These parameters were subsequently employed to evaluate  $H^E$  data at other value of  $x_i$ . Such  $H^E$  data alongwith  $X_A$  and  $X'$  are recorded in Table 3 and are also compared with their experimental values. Examination of Table 3 shows that  $H^E$  data compare well with the corresponding experimental values. This lends support to the assumption made in deriving Eq. 13 and also to the validity of assumption  $V_j/V_i = {}^3\xi_i/{}^3\xi_j$ .

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