MOLECULAR INTERACTIONS IN BINARY MIXTURES OF NON-ELECTROLYTES: MOLAR EXCESS ENTHALPIES

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(Received 27 December 1984)

ABSTRACT

Molar excess enthalpies, H^E, for pyridine (i) + α-picoline (j), + β-picoline (j), + γ-picoline (j); pyridine (i) + cyclohexane (j); β-picoline (i) + cyclohexane (j); methylenebromide (i) + pyridine (j), + β-picoline (j) mixtures have been measured calorimetrically as a function of temperature and composition. The H^E data at 298.15 and 308.15 K have been analysed in terms of the Sanchez and Lacombe theory and the "graph theoretical approach". The graph theoretical approach describes the H^E data well for all these mixtures. This approach has been critically examined and it is found to provide an insight into the nature of molecular interactions between the components of these mixtures. NMR studies on methylene bromide (i) + β-picoline (j) and β-picoline (i) + pyridine (j) further support these conclusions.

INTRODUCTION

A graph theoretical approach has recently been developed [1–3] to explain molar excess volumes and molar excess enthalpies of binary mixtures of non-electrolytes. Since thermodynamic excess functions are a measure of solute (j)–solvent (i) interactions and as an $(i + j)$ binary mixture may be assumed to have been formed by the replacement of like contacts in the pure i and j component by unlike $(i–j)$ contacts in the mixture, it appears that the graph theoretical approach could also be utilized to observe the nature of molecular interactions between i and j in the $(i + j)$ mixture. Further, Sanchez and Lacombe have proposed a theory of fluid mixtures [4,5] and it would be interesting to examine the performance of these theories in explaining H^E data of binary mixtures of non-electrolytes containing a heterocyclic, like pyridine.

EXPERIMENTAL

Pyridine, α-picoline, β-picoline, γ-picoline, cyclohexane and methylene-bromide (all BDH, Analar grade) were purified by standard methods [6]. The

purities of the final samples were checked by determining their densities at 298.15 ± 0.01 K and these agreed to within 0.00005 g cm^{-3} with the corresponding literature values [7–10].

Molar excess enthalpies, H^E_{ij}, were measured calorimetrically by a method described earlier [11]. The temperature of the bath was controlled to ± 0.01 K by means of a toluene regulator and the uncertainty in the measured H^E_{ij} values is about 1%.

Samples for NMR studies were prepared by mixing (by weight) methylenebromide with β-picoline, and β-picoline with pyridine in the NMR tubes followed by dilution with a fixed quantity of an inert solvent (cyclohexane). Immediately after preparation a fixed quantity of tetramethylsilane (TMS) (used as internal reference) was added to each tube and the chemical shift of methylenebromide, or of the CH$_3$ proton of β-picoline relative to TMS, was detected on a 90 MHz spectrometer using the side band method [12]. The chemical shifts for the various mixtures were averaged over three determinations and were reproducible to ± 0.5 Hz.

RESULTS

Molar excess enthalpies, $H^E_{ij}(T_1, x_i)$, for the various $(i + j)$ binary mixtures as a function of composition at 298.15 and 308.15 K (reported in Table 1) were fitted to the equation

$$H^E_{ij}(T, x_i)/\text{J mol}^{-1} = x_i(1 - x_i)\left[H^0_{ij} + H'_{ij}(2x_i - 1) + H^2_{ij}(2x_i - 1)^2\right] \quad (1)$$

where H^n_{ij} ($n = 0$–2) are disposable parameters and x_i is the mole fraction of component i in the binary mixture. These parameters were evaluated by fitting $H^E_{ij}(T, x_i)/x_i(1 - x_i)$ to eqn. (1) by the method of least squares and are recorded, together with the standard deviations, σ (H^E_{ij}), of $H^E_{ij}(T, x_i)$ defined by

$$\sigma\left(H^E_{ij}\right)/\text{J mol}^{-1} = \left\{\frac{\Sigma\left[H^E_{ij}(T, x_i)_{\text{exp.}} - H^E_{ij}(T, x_i)_{\text{calc.eqn.(1)}}\right]^2}{m - t}\right\}^{0.5} \quad (2)$$

(where m is the number of data points and t is the number of adjustable parameters in eqn. (2)) in Table 2.

DISCUSSION

The experimental H^E_{ij} values for pyridine $(i) + \alpha$-picoline (j), $+ \beta$-picoline (j), $+ \gamma$-picoline (j); pyridine $(i) +$ cyclohexane (j); and β-picoline $(i) +$ cyclohexane (j) mixtures are all positive, while they are negative for methylenebromide $(i) +$ pyridine (j) and $+ \beta$-picoline (j) mixtures at both

TABLE 1

Measured molar excess enthalpies, H_{ij}^E (J mol^{-1}) for various $(i + j)$ mixtures at 298.15 and 308.15 K

x_i	H_{ij}^E	x_i	H_{ij}^E
Pyridine (i) + α-picoline (j) at 298.15 K			
0.1202	36.5	0.5596	81.9
0.1673	49.0	0.6653	69.2
0.2031	56.7	0.7554	54.0
0.2988	74.0	0.8333	37.9
0.4157	83.7	0.9183	18.2
0.5516	82.5		
At 308.15 K			
0.0979	9.1	0.5442	46.0
0.2012	21.0	0.6618	41.5
0.2550	26.7	0.7704	30.5
0.3313	34.9	0.8727	18.3
0.4276	41.3		
Pyridine (i) + β-picoline (j) at 289.15 K			
0.1170	23.3	0.4755	43.0
0.1498	28.4	0.5798	38.5
0.2652	39.0	0.7116	30.8
0.3127	40.5	0.8412	20.2
At 308.15 K			
0.1310	16.0	0.6213	37.4
0.1345	16.5	0.6813	33.5
0.2014	24.0	0.7523	27.0
0.2950	33.1	0.8039	22.2
0.4645	40.5	0.8132	21.3
0.4885	41.3	0.8804	13.1
0.5484	40.2		
Pyridine (i) + γ-picoline (j) at 298.15 K			
0.0673	19.1	0.6002	53.2
0.1618	38.0	0.6936	47.1
0.2222	45.8	0 7792	38.7
0.2900	51.0	0.8600	28.0
0.3841	56.0	0.8636	26.4
0.4667	56.0	0.9255	15.9
0.5328	55.1		
At 308.15 K			
0.0632	17.9	0.5170	58.5
0.1224	31.2	0.5915	54.1
0.1773	41.1	0.6884	44.8
0.2636	52.6	0.7736	35.8
0.2935	54.9	0.8241	27.8
0.3472	58.1	0.8831	19.6
0.4254	61.0	0.9452	10.0

TABLE 1 (continued)

x_i	H_{ij}^{E}	x_i	H_{ij}^{E}
Pyridine (i) + cyclohexane (j) at 298.15 K			
0.0854	539.4	0.4815	1393.4
0.1489	831.9	0.5269	1390.2
0.1757	930.5	0.6019	1316.9
0.2000	1020.4	0.7002	1152.4
0.2662	1200.0	0.7852	943.6
0.3486	1338.6	0.8714	630.5
0.4112	1390.1	0.8954	548.6
At 308.15 K			
0.0759	478.3	0.4892	1381.4
0.1614	876.0	0.5676	1311.8
0.2450	1143.4	0.5879	1294.3
0.3333	1320.2	0.6235	1232.0
0.3563	1334.1	0.6691	1161.2
0.4024	1372.4	0.7018	1068.8
0.4155	1379.6	0.8796	507.8
β-Picoline (i)+cyclohexane (j) at 298.15 K			
0.0444	272.0	0.5125	1306.0
0.1081	596.2	0.6021	1204.9
0.1983	940.1	0.6662	1100.0
0.2841	1170.0	0.7326	940.0
0.3873	1316.9	0.7878	786.0
0.4340	1330.1	0.8854	450.0
At 308.15 K			
0.0857	370.0	0.5714	1280.9
0.1768	728.1	0.6200	1205.0
0.3077	1120.6	0.6800	1080.2
0.3367	1180.7	0.7315	961.9
0.4519	1307.6	0.8555	557.4
0.4688	1324.3	0.9300	272.1
Methylenebromide (i) + pyridine (j) at 298.15 K			
0.1154	-245.3	0.5159	-474.9
0.1589	-305.8	0.6059	-430.1
0.2245	-385.9	0.6755	-383.5
0.3312	-465.1	0.7862	-272.6
0.4202	-486.0	0.9318	-100.1
0.4898	-484.3		
At 308.15 K			
0.0788	-138.7	0.5478	-496.2
0.1724	-288.8	0.6284	-467.2
0.2554	-375.3	0.6970	-428.8
0.3247	-432.0	0.7448	-378.5
0.3914	-480.0	0.8221	-296.5
0.4643	-497.0	0.9026	-179.1
Methylenebromide (i)+ β-picoline (j) at 298.15 K			
0.1120	-249.2	0.5201	-700.1
0.1739	-377.7	0.6043	-655.8

TABLE 1 (continued)

x_i	H_{ij}^E	x_i	H_{ij}^E
0.2342	−485.2	0.6581	−615.2
0.3215	−610.0	0.7143	−545.3
0.4000	−682.3	0.8103	−388.3
0.4348	−689.7	0.9005	−208.3
At 308.15 K			
0.0842	−130.9	0.5000	−281.0
0.1460	−202.2	0.5956	−256.7
0.2012	−238.0	0.6555	−240.2
0.2712	−272.1	0.7114	−219.8
0.3415	−290.0	0.8018	−171.2
0.4235	−286.8	0.9234	−79.9

temperatures. Further, the H_{ij}^E values at 298.15 K for an equimolar composition of pyridine (i) + α-picoline (j), +β-picoline (j) and +γ-picoline (j) mixtures vary in the order α-picoline > β-picoline > γ-picoline, but it varies in the order pyridine > β-picoline for methylenebromide (i) or cyclohexane (i) + pyridine (j) and +β-picoline (j) mixtures. Again, while $\partial H_{ij}^E/\partial T$ for pyridine (i) +α-picoline (j) and +β-picoline (j) mixtures is negative, it is positive for pyridine (i) + γ-picoline (j). However, while ($\partial H_{ij}^E/\partial T$) for methylenebromide ($i$) + pyridine ($j$) is negative, it is positive for methylenebromide (i) +β-picoline (j) mixtures. ($\partial H_{ij}^E/\partial T$) for cyclohexane ($i$) + pyridine ($j$) and +β-picoline ($j$) mixtures, however, varies, in an opposite way to that of methylenebromide (i) +pyridine (j) and +βpicoline (j) mixtures.

H_{ij}^E data for methylenebromide (i) +pyridine (j) and +β-picoline (j) mixtures may be explained by assuming that these mixtures are characterized by specific electron donor–acceptor interactions between methylenebromide (electron acceptor) and pyridine (j) and β-picoline (j) (electron donors), and that there is a steric repulsion between the components of these mixtures.

If the methylenebromide (i) +pyridine (j) mixture is assumed to be characterized by charge-transfer interactions between the π-electron cloud of the aromatic ring of pyridine (or the lone pair of electrons on the nitrogen atom in pyridine) and the empty $3d$ levels of the bromine atoms of methylenebromide, the introduction of a −CH_3 substituent at the β-position in pyridine, as in β-picoline, would render the π-electron cloud of the aromatic ring in β-picoline (or the lone pair of electrons on the nitrogen atom in β-picoline) to be more labile so that, compared to pyridine, β-picoline would interact strongly with methylenebromide. At the same time the close proximity of the −CH_3 substituent on β-picoline with the bromine atoms of methylenebromide would increase the steric repulsion between

TABLE 2

H^n ($n = 0-2$) parameters of eqn. (1) and standard deviations, $\sigma(H)^E$, for the various mixtures

Mixture	Temp. (K)	H^0 (J mol^{-1})	H^1 (J mol^{-1})	H^2 (J mol^{-1})	$\sigma(H)^E$ (J mol^{-1})
Pyridine (i)	298.15	340	-59.5	-71.4	0.34
+ α-picoline (j)	308.15	180	35.7	-83.3	0.55
Pyridine (i)	298.15	168	-53.6	36.3	0.48
+ β-picoline (j)	308.15	164	-5.9	57.7	0.45
Pyridine (i)	298.15	224	-35.7	58.3	0.55
+ γ-picoline (j)	308.15	236	-71.4	13.1	0.55
Pyridine (i)	298.15	5600	-595.2	1011.9	7.8
+ cyclohexane (j)	308.15	5520	-1071.4	321.4	9.1
β-Picoline (i)	298.15	5280	-1071.4	35.7	5.3
+ cyclohexane (j)	308.15	5280	-357.1	-1154.8	6.0
Methylenebromide (i)	298.15	-1920	535.7	-53.6	3.2
+ pyridine (j)	308.15	-2000	0.0	0.0	4.6
Methylenebromide (i)	298.15	-2800	119.0	535.7	5.3
+ β-picoline (j)	308.15	-1120	345.2	-470.2	2.3

them. If β-picoline orients itself in such a way that its $-CH_3$ substituent lies further away from the bromine atoms of methylenebromide, the contribution to H^E due to steric repulsion between β-picoline and methylenebromide would be very small compared to the specific interactions between them. The fact that H^E_{ij} values for methylenebromide (i) + β-picoline (j) are less than the corresponding H^E_{ij} values for methylenebromide (i) + pyridine (j) mixtures supports this scheme of molecular interactions. Further, since $(\partial H^E_{ij}/\partial T)$ for methylenebromide (i) + β-picoline (j) mixture is positive, it is suggested that the specific interactions between the components of these mixtures, get weaker as the temperature is raised. On the other hand, since H^E_{ij} for the methylenebromide (i) + pyridine (j) mixture is also negative, and as it becomes even more negative as the temperature is raised, it is suggested that an increase in temperature favours specific interactions between the components of this mixture. The fact that the experimental H^E_{ij} values for cyclohexane (i) + pyridine (j) and + β-picoline (j) mixtures are positive and vary in the order pyridine > β-picoline, further suggests that methylenebromide (i) + pyridine (j) and + β-picoline (j) mixtures are characterized by specific interactions between their components and that steric factors also contribute to the measured H^E_{ij} values of these mixtures. Again, since $\partial H^E/\partial T$ for the cyclohexane (i) + pyridine (j) mixture is negative, this may be taken to suggest that β-picoline might interact with cyclohexane by dipole–induced-dipole interactions.

The $H^E_{ij}(T, x_i)$ data at 298.15 and 308.15 K for the various binary mixtures were next analysed in terms of the Sanchez and Lacombe theory of

fluid mixtures [4,5]. $H_{ij}^{E}(T,x_i)$ for a binary $(i+j)$ mixture according to this theory [4] are given by

$$H_{ij}^{E}(T,x_i) = 2\phi_i\phi_j r_{mix}\bar{\rho}_{mix}\left(\epsilon_{ii}^{*} + \epsilon_{jj}^{*} - 2\epsilon_{ij}^{*}\right) + RTr_{mix}\Sigma\frac{\left(\phi_i^0\bar{\rho}_i - \phi_i\bar{\rho}_{mix}\right)}{\bar{T}_i} \qquad (3)$$

$$\phi_i = m_i\left(\rho_i^{*}\right)^{-1}\Sigma\left(m_i/\rho_i^{*}\right)^{-1} \qquad (4)$$

$$m_i = x_i M_i\left(\Sigma x_i M_i\right)^{-1} \qquad (5)$$

$$r_{mix} = \Sigma x_i r_i \qquad (6)$$

$$r_i = r_i^0\left[V_i^{*}\left(V_{mix}^{*}\right)^{-1}\right] \qquad (7)$$

$$v_{mix}^{*} = \phi_i v_i^{*} \qquad (8)$$

$$\phi_i^0 = m_i\left(\rho_i^{*}v_i^{*}\right)^{-1}/\left[\Sigma\left(m_i/\rho_i^{*}v_i^{*}\right)\right] \qquad (9)$$

$$\tilde{V}_{mix} = 1/\bar{\rho}_{mix} \qquad (10)$$

where all the terms have the same significance as described by Sanchez and Lacombe [4,5]. Evalution of $H_{ij}^{E}(T,x_i)$ by this theory, therefore, requires a knowledge of the reduced density, $\bar{\rho}_{mix}$, of the mixture, which, in principle, can be evaluated from the equation of state of the mixture, i.e.

$$\left(\bar{\rho}_{mix}\right)^2 + \left(RT/\epsilon_{mix}^{*}\right)\left[\bar{\rho}_{mix}\left(1 - r_{mix}^{-1}\right) + \ln(1 - \bar{\rho}_{mix})\right] + \bar{P} = 0 \qquad (11)$$

where

$$\epsilon_{mix}^{*} = \sum_i \phi_i\epsilon_{ii}^{*}RT\sum\sum\phi_i\phi_j\bar{X}_{ij} \qquad (12)$$

$$\bar{X}_{ij} = \left(\epsilon_{ii}^{*} + \epsilon_{jj}^{*} - 2\epsilon_{ij}^{*}\right)/RT \qquad (13)$$

$$\bar{P} = PV_{mix}^{*}/\epsilon_{mix}^{*} \qquad (14)$$

provided the interaction energy, ϵ_{ij}^{*}, for the $(i+j)$ mixture is known. Since such information is not available in most cases, the interaction energy, ϵ_{ij}^{*} (which was assumed to be independent of composition for the $(i+j)$ mixture), was calculated from the $H_{ij}^{E}(T,x_i = 0.5)$ datum of an $(i+j)$ mixture through eqns. (3)–(10). This value of ϵ_{ij}^{*} was then employed to evaluate $\bar{\rho}_{mix}$ and, hence, $H_{ij}^{E}(T,x_i)$ data for the $(i+j)$ mixture through eqns. (3)–(10). Such $H_{ij}^{E}(T_1,x_i)$ data for the various binary mixtures are recorded as "H^E Calc. (1)" in Table 3 and are also compared with their corresponding experimental values. In all these calculations the necessary parameters for the components of $(i+j)$ mixtures were taken from the literature [4] while those for methylenebromide were evaluated from its vapour pressure [12] and density data [9] at different temperatures in the manner suggested by Sanchez and Lacombe [4].

Examination of Table 3 clearly shows that the $H_{ij}^{E}(T,x_i)$ values thus calculated at 298.15 and 308.15 K fail to reproduce the experimental

TABLE 3

Comparison of calculated H_{ij}^E values with their corresponding experimental values for various $(i+j)$ mixtures

System	Temp. (K)	$^3\xi_i/^3\xi_j$	χ_{ij} (J mol^{-1})	K_{ij}		H_{ij}^E (J mol^{-1})			
						$x_i = 0.1$	0.3	0.7	0.9
Pyridine (i) + α-picoline (j) (ξ = 0.9979)	298.15	0.695 (0.792)	344.74	1.1084 (0.9738)	Calc.(1)	–	1629.1	2342.9	–
					Calc.(2)	–	–44.3	184.1	–
					Exp.	30.0	72.2	64.8	26.3
					Calc.(3)	29.4(30.9)	69.9(71.8)	72.9(71.0)	31.9(38.2)
	308.15		127.63	2.725 (2.4825)	Calc.(1)	–	1609.1	2332.4	–
					Calc.(2)	–	30.5	161.2	–
					Exp.	11.4	31.6	38.9	24.0
					Calc.(3)	11.8(12.2)	31.9(32.5)	46.4(45.2)	25.7(24.1)
Pyridine (i) + β-picoline (j) (ξ = 0.9979)	298.15	0.682 (0.792)	218.34	0.7261 (0.6254)	Calc.(1)	–	72.3	72.3	–
					Calc.(2)	–	28.7	28.7	–
					Exp.	19.0	41.2	32.4	14.1
					Calc.(3)	17.2(18.5)	37.6(38.9)	33.2(32.3)	13.5(12.8)
	308.15		142.63	1.5674 (1.3528)	Calc.(1)	–	37.8	30.5	–
					Calc.(2)	–	37.8	30.5	–
					Exp.	13.4	33.5	31.9	14.8
					Calc.(3)	12.5(13.2)	31.6(32.5)	37.8(36.6)	17.9(16.8)
Pyridine (i) + γ-picoline (j) (ξ = 0.9975)	298.15	0.668 (0.792)	245.87	0.9924 (0.8369)	Calc.(1)	–	634.6	857.7	–
					Calc.(2)	–	56.7	66.2	–
					Exp.	27.0	52.3	45.7	20.4
					Calc.(3)	20.3(21.7)	47.2(48.8)	46.9(45.4)	21.0(18.8)
	308.15		289.76	0.8149 (0.6872)	Calc.(1)	–	61.8	68.0	–
					Calc.(2)	–	61.8	68.0	–
					Exp.	27.2	56.3	45.9	20.6
					Calc.(3)	23.2(24.9)	51.8(53.5)	47.5(46.1)	19.6(18.5)

System	T/K								
Pyridine (i) + cyclohexane (j) (ξ = 0.9979)	298.15	0.377 (1.0)	6500.28	2.0056 (0.7567)	Calc.(1)	—	33.2	35.2	—
					Calc.(2)	—	9477.5	1624.2	—
					Exp.	620.1	1260.4	1160.9	480.3
					Calc.(3)	397.1(566.8)	1036.5(1244.9)	1358.9(1114.3)	689.6(453.7)
	308.15		6879.40	1.7757 (0.67)	Calc.(1)	—	2158.5	2910.6	—
					Calc.(2)	—	1064.7	1319.7	—
					Exp.	660.5	1280.2	1080.0	460.1
					Calc.(3)	406.0(590.1)	1042.7(1258.7)	1305.1(1074.3)	639.8(428.9)
β-Picoline (i) + cyclohexane (j) (ξ = 0.9798)	298.15	0.553 (1.263)	7601.21	1.2144 (0.5375)	Calc.1	—	130.7	645.9	—
					Calc.(2)	—	937.6	1486.3	—
					Exp.	610.9	1200.6	1040.3	430.7
					Calc.(3)	441.5(628.8)	1068.1(1263.1)	1152.8(988.1)	514.5(381.9)
	308.15		14515.45	0.5073 (0.2246)	Calc.(1)	—	2859.9	3211.4	—
					Calc.(2)	—	1101.3	1198.3	—
					Exp.	510.8	1100.6	1040.3	430.0
					Calc.(3)	644.3(967.8)	1276.2(1487.3)	980.2(883.9)	376.4(314.9)
Methylenebromide (i) + pyridine (j) (ξ = 1.018)	298.15	1.767 (0.667)	−2048.07	0.333 (0.8823)	Calc.(1)	—	620.3	217.9	—
					Calc.(2)	—	−342.6	−392.5	—
					Exp.	−190.0	−390.2	−340.6	−150.9
					Calc.(3)	−287.7(−181.9)	−503.8(−143.5)	−336.1 (−393.4)	−123.5(−164.6)
	308.15		−1666.67	0.566 (1.5)	Calc.(1)	—	613.8	−389.7	—
					Calc.(2)	—	296.5	−389.7	—
					Exp.	−155.2	−400.0	−430.3	−200.7
					Calc.(3)	−213.3(−155.2)	−472.4(−388.9)	−378.1 (−456.5)	−147.3(−214.3)
Methylenebromide (i) + β-picoline (j) (ξ = 1.007)	298.15	1.205 (0.528)	−2145.5	0.823 (1.8779)	Calc.(1)	—	1030.8	2437.9	—
					Calc.(2)	—	−484.8	−647.4	—
					Exp.	−240.0	−500.4	−570.4	−200.6
					Calc.(3)	−273.4(−176.9)	−611.9(−353.9)	−565.9 (−275.2)	−233.7(−106.1)

TABLE 3 (continued)

System	Temp. (K)	$^3\xi_i/^3\xi_j$	χ_{ij} (J mol^{-1})	K_{ij}		H_{ij}^E (J mol^{-1})			
						$x_i=0.1$	0.3	0.7	0.9
	308.15		-1193.67	0.387 (0.8837)	Calc.(1)	–	635.2	2114.8	–
					Calc.(2)	–	-191.8	-238.8	–
					Exp.	-150.8	-280.9	-240.7	-100.3
					Calc.(3)	-155.3(-82.3)	-285.3(-130.7)	-200.1(-79.8)	-74.6(-28.6)
Chloroform (i) +1,4-dioxane (j)	303.15	1.344	-5520.2	1.929					
Chloroform (i) + diethylether (j)	298.15	2.45	-10422.9	0.444					
Chloroform (i) + pyridine (j)	308.15	1.766	-5958.2	1.036					
Chloroform (i) + α-picoline (j)	308.15	1.288	-9165.5	1.342					
Chloroform (j) + γ-picoline (j)	308.15	1.18	-8102.3	1.384					

$H_{ij}^E(T, x_i)$ for almost all the $(i + j)$ mixtures studied here. This failure of the theory may be traced to the assumption that all these $(i + j)$ mixtures satisfy eqn. (11). It is therefore essential to know the extent to which these $(i + j)$ mixtures deviate from this basic equation. For this purpose, H_{ij}^E $(x = 0.5)$ and V_{ij}^E $(x_i = 0.5)$ data at 308.15 K for an $(i + j)$ mixture were employed to calculate $\bar{\rho}_{mix}$, ϵ_{ij}^* and, hence, the right-hand side of eqn. (11). It was found that the right-hand side of eqn. (11) varied from 0.01 to 0.051 for these binary mixtures. Once the right-hand side of eqn. (11) was thus established for a binary mixture the reduced density, $\bar{\rho}_{mix}$, for that mixtures at any other composition or temperature was calculated by solving eqn. (11) by a numerical technique. This value of $\bar{\rho}_{mix}$ was then employed to calculate $H_{ij}^E(T, x_i)$. Such H_{ij}^E values at 298.15 and 308.15 K are recorded as "H_{ij}^E calc. (2)" in Table 3 and are also compared with their corresponding experimental values. Examination of Table 3 now reveals that the $H_{ij}^E(T_1, x_i)$ values as calculated from the Sanchez and Lacombe theory, although they considerably improve the situation, do not make a very impressive agreement with their corresponding experimental values. The failure of this theory to reproduce the experimental H_{ij}^E data for all the $(i + j)$ mixtures studied here may then be due to the assumption that the right-hand side of eqn. (11) does not vary with composition.

It would now be interesting to see how ϵ_{ij}^* of a binary $(i + j)$ mixture (as evaluated in the manner described above) deviates from the geometric mean of ϵ_{ii}^* and ϵ_{jj}^*.

If ξ is the extent to which ϵ_{ij}^* deviates from $(\epsilon_{ii}^* + \epsilon_{jj}^*)^{1/2}$ then

$$\xi = \epsilon_{ij}^* / (\epsilon_{ii}^* + \epsilon_{jj}^*)^{1/2} \tag{15}$$

such ξ values for the various binary mixtures are recorded in Table 3 and show that whereas ξ for the methylenebromide (i) + pyridine (j) mixture is 1.08, it changes to 1.007 for the methylenebromide (i) + β-picoline (j) mixture. Further, whereas $\xi = 0.9979$ for pyridine (i) + α-picoline (j), + β-picoline (j), and + γ-picoline (j) mixtures, $\xi = 0.978$ and 0.98, respectively, for pyridine (i) + cyclohexane (j) and β-picoline (i) + cyclohexane (j) mixtures. Since $\xi > 1$ suggests that $(i-j)$ interactions are stronger than the $i-i$ or $j-j$ interactions, the ξ values suggest that methylenebromide (i) + pyridine (j) and methylenebromide (i) + β-picoline (j) mixtures are characterised by weak specific interactions between their components and that the unlike interactions become weaker when pyridine is replaced by β-picoline in their binary mixtures with methylenebromide. The ξ values for pyridine (i) + α-picoline (j), + β-picoline (j), and + γ-picoline (j) mixtures, on the other hand, suggest that the unlike interactions in all these mixtures are weaker than the like interactions and that α-, β- and γ-picolines are almost identical in their interactions with pyridine. The same may also be true of pyridine (i) + cyclohexane (j) and β-picoline (i) + cyclohe-

xane (j) mixtures. This suggests that α-, β- and γ-picolines are involed in $\pi-\pi$ type interactions with pyridine.

$H_{ij}^E(T_1, x_i)$ data were next analysed in terms of the graph theoretical approach [2]. $H_{ij}^E(T, x_1)$ according to this approach is given by

$$H_{ij}^E(T, x_i) = \frac{x_i(1 - x_i)\chi_{ij}K_{ij}\left(^3\xi_i/^3\xi_j\right)}{x_i + (1 - x_i)K_{ij}\left(^3\xi_i/^3\xi_j\right)} \tag{16}$$

where

$$^3\xi_i = \sum_{l<m}\sum_{m<n}\sum_{n<o}\left(\delta_l\delta_m\delta_n\delta_o\right)^{-0.5} \tag{17}$$

denote the connectivity index of the third degree of the ith molecule and δ_l, etc., represent the degree of the lth, etc., vertices in the molecular graph of i. χ_{ij} is the interaction energy per i–j contact and K_{ij} has its usual significance [2].

Evaluation of $H_{ij}^E(T, x_i)$ data for a binary $(i + j)$ mixture thus requires a knowledge of its χ_{ij} and K_{ij} parameters provided the $^3\xi$ values of the constituents of a binary mixture are known. The $^3\xi$ values could be evaluated from eqn. (17) utilizing either δ [1,2] or δ^v [3] (valence δ, which explicitly reflects the valency of the atoms forming the bonds in the molecule) considerations. The use of δ considerations to evaluate $^3\xi$ values of a molecular entity however, would fail to differentiate, say, benzene from cyclohexane or pentane from pent-1-ene. To overcome this problem, Singh [3] advocated the use of δ^v rather than δ values to evaluate $^3\xi$ values of the consitutents of the binary mixture. Such a procedure would also be conducive to quantify the information contained in the molecular graphs of such molecules as alkanols, esters, ethers, etc., which is not possible when their $^3\xi$ values are evaluated using δ values of the vertices of their molecular graphs. However, the use of $H_{ij}^E(T_1, x_i$ say, 0.4 and 0.5) data to evaluate χ_{ij} and K_{ij} through eqn. (16) and their subsequent use in this equation to evaluate $H_{ij}^E(T, x_i)$ at any x_i at that temperature makes the use of $^3\xi$ values of the constituents of the redundant mixture. Consequently, while the $H_{ij}^E(T_1, x_i)$ data evaluated for the $(i + j)$ mixture from eqn. (16) through use of $H_{ij}^E(T_1, x_i = x_i'$ and $x_i'')$ data would be a function of x_i', x_i'' and $H_{ij}^E(T_1, x_i'$, $x_i'')/H_{ij}^E(T_1, x_i', x_i'')$ only, the χ_{ij} value evaluated from eqn. (16) would be independent of x_i' and x_i'' and would depend on $H_{ij}^E(T_1, x_i = x_i'$ and $x_i'')$ data alone. Nevertheless, the $H_{ij}^E(T_1, x_i)$ values calucated for the various binary mixtures reproduce their experimental $H_{ij}(T_1, x_i)$ data well, as is evident from Table 3. In order to illustrate the versatility of the graph theoretical approach in understanding the nature of molecular interactions between the components of binary mixtures, it would be interesting to examine the influence of $^3\xi$ values of the constituents of the binary mixtures on their K_{ij} values.

For this purpose we evaluated χ_{ij} and K_{ij} ($^3\xi_i/^3\xi_j$) parameters from eqn. (16) utlizing $H^E_{ij}(T, x_i = 0.4$ and 0.5) data for $(i+j)$ mixtures. The $K_{ij}(^3\xi_i/^3\xi_j)$ values were next employed to yield K_{ij} values for the $(i+j)$ mixture when $^3\xi$ parameters of i and j molecular entities were evaluated from δ [1,2] or δ^v [3] considerations. Such K_{ij} values are recorded in Table 3 (the values in parentheses are the values corresponding to the use of $^3\xi$ values derived from δ considerations of the vertices of the molecular graph concerned). Table 3 also contains $^3\xi_i/^3\xi_j$ values based on δ or δ^v considerations for the various binary mixtures (values in parentheses are those obtained from $^3\xi$ values evaluated from δ considerations).

Equation (16) was derived on the assumption that the number of effective i–j contacts in a binary $(i+j)$ mixture is determined primarily by that part of the molar volumes of i and j that determine their tendency to allow their surface areas to come into effective contact with each other. Since a molecule allows only a part of its surface area to come into effective contact with the surface area of another molecule, and since $^{1/3}\xi$ of a molecule was taken to be a measure of this tendency of the molecule, V_j/V_i in a binary mixture was expressed as

$$V_j/V_i = K_{ij}\left(^3\xi_i/^3\xi_j\right)$$

Since ($^3\xi_i/^3\xi_j$) measures the relative tendencies of the ith and jth molecule (in a binary $(i+j)$ mixture) to discriminate their surface areas in i–j contacts, K_{ij} is a measure of the extent to which these discriminating molecules come into effective i–j contacts.

Before analysing the K_{ij} and χ_{ij} data of the various binary mixtures reported in Table 3, it would be illuminating to examine the K_{ij} and χ_{ij} data evaluated from eqn. (16) for some typical mixtures in the literature [3]. Such data are also recorded in Table 3.

From their analysis of the G^E and H^E data of chloroform (i) + 1,4-dioxane (j) mixtures in terms of the ideal, associated model approach, McGlashan and Rastogi [13] inferred that this mixture is characterized by the following two equilibria

$$i+j \rightleftharpoons i:j$$

$$i+j \rightleftharpoons 1:2j$$
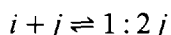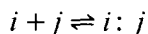
and that the enthalpy of $i:j$ and $i:2j$ molecular complexes in this mixture is $\Delta h_i = -8.4$ and $\Delta h_2 = -15$ kJ mol^{-1}, respectively. These workers had further informed that if 1,4-dioxane is replaced by diethylether in its binary mixture with $CHCl_3$ (i), the enthalpy of formation of the $CHCl_3$: diethylether molecular complex would be twice that of the enthalpy of formation of the $CHCl_3$: 1,4-dioxane molecular complex.

($^3\xi_i/^3\xi_j$) for $CHCl_3$ (i) + 1,4-dioxane (j) is 1.344 [3] (based on δ^v considerations) which indicates that 1,4-dioxane (j) does not allow its entire surface area to come into effective i–j contact with i, and since K_{ij} for this

mixture is 1.929 (≈ 2.0) [3] it is suggested that 1,4-dioxane (i) forms two types of (i–j) contacts with i in this mixture. This is consistent with the equilibria expressed by eqns. (18) and (19). The χ_{ij} value of -5.52 kJ mol^{-1} at 303.15 K evaluated for this mixture from eqn. (16) (using δ^v considerations) appears to be some sort of average of the Δh_1 and Δh_2 values calculated for this mixture from an analysis of its H^E and G^E data in terms of the ideal associated model approach. Further, ($^3\xi_i/^3\xi_j$) and K_{ij} for CHCl$_3$ (i) + diethylether (j) is ≈ 2.5 [3] and 0.444 (≈ 0.5) [3] at 298.15 K, respectively. This would then mean that the highly discriminating diethylether (j) forms only one i–j contact with i and that only a small part of its jth surface area is involved in these i–j contacts. This is possible if diethylether (j) allows only the oxygen atom of its $>$C=O group to form a hydrogen bond with CHCl$_3$ (i). This, however, is consistent with NMR studies of the CHCl$_3$ (i) + pyridine (j) mixture. The Δh_1 value (-10.42 kJ mol^{-1}) [3] for CHCl$_3$ (i) + diethylether (j) is nearly twice that of χ_{ij} (-5.52 kJ mol^{-1}) [3] for CHCl$_3$ (i) + 1,4-dioxane (j) mixtures. Similarly, the ($^3\xi_i/^3\xi_j$) and K_{ij} values [3] for CHCl$_3$ (i) + pyridine (j), + α-picoline (j) and + γ-picoline (j) mixtures suggest that the j element is the discriminating entity in all these mixtures and that probably one type of i–j contact is formed in them.

We now examine the ($^3\xi_i/^3\xi_j$), K_{ij} and χ_{ij} data reported for the various mixtures in Table 3.

Pyridine (i) and β- and γ-picolines (j) act as both N and π-electron donors. Consequently, in the present ($i + j$) mixture, i should be the discriminating entity. This is aptly evident if ($^3\xi_i/^3\xi_j$) values based on δ^v considerations are considered. The use of $^3\xi$ values based on δ^v considerations to evaluate K_{ij} for the ($i + j$) mixture also clearly differentiate CH$_2$Br$_2$ (i) + pyridine (j) and + β-picoline (j) mixtures form the rest of the ($i + j$) mixtures. This is also consistent with the observed H_{ij}^E data of these mixtures. However, the use of $^3\xi$ values based on δ or δ^v considerations to evaluate ($^3\xi_i/^3\xi_j$) and K_{ij} values for pyridine (i) + α-picoline (j), + β-picoline (j) and + γ-picoline (j) mixtures suggests that $^3\xi$ values based on both the δ and δ^v considerations yield almost identical results for these mixtures. The K_{ij} and χ_{ij} values of CH$_2$Br$_2$ (i) + pyridine (j) and CH$_2$Br$_2$ (i) + β-picoline (j) mixtures at 298.15 K also suggest that these mixtures are characterized by weak specific interactions between the components of these mixtures and probably a 1:1 molecular complex is present in them. NMR studies of these mixtures (in the following paragraphs) lend further credence to such a conjecture. The values for CH$_2$Br$_2$ (i) + pyridine (j) and CH$_2$Br$_2$ (i) + β-picoline (j) further indicate that, compared to pyridine, β-picoline should interact strongly with CH$_2$Br$_2$. This is as expected.

This suggests that perhaps it is the C–C skeletal interactions that determine the thermodynamic excess functions of pyridine (i) + α-picoline (j), + β-picoline (j), and + γ-picoline (j) mixtures. On the other hand, the

TABLE 4

Proton resonance shifts (δ) of various ($i + j$) mixtures with respect to pure component i

Mole fraction of component i	δ (Hz)
Methylenebromide (i)+β-picoline (j) (δ_∞ = 58.5 Hz)	
0.0369	56.70
0.1012	54.00
0.2241	46.01
0.3921	36.19
0.5293	28.80
β-Picoline (i)+pyridine (j)	
0.0512	2.65
0.1482	1.80
0.2720	1.60
0.3404	0.90

valency of individual atoms in the "molecular graph" of methylenebromide, pyridine and β-picoline may govern the thermodynamic excess functions of methylene bromide (i) +pyridine (j) and +β-picoline (j) mixtures.

In order to further investigate the nature of molecular interactions in methylenebromide (i) +β-picoline (j) and β-picoline (i) +pyridine (j) mixtures, we studied the proton chemical shifts of methylenebromide and β-picoline protons relative to pure methylenebromide and β-picoline in these ·($i + j$) mixtures.

The proton chemical shift, δ, of methylenebromide in β-picoline and that of the $-CH_3$ protons of β-picoline in pyridine relative to pure methylenebromide and β-picoline, respectively, are recorded in Table 4.

It is quite evident from Table 4 that, while there is a large net shift (which may be termed as the internal shift) of $-CH_3$ protons of β-picoline in pyridine towards higher magnetic fields, the chemical shift of methylenebromide protons in β-picoline is shifted towards low magnetic fields. A partial explanation of the former proton chemical shift may be sought in the large diamagnetic anisotropy of pyridine.

Pyridine has a π-electron cloud both above and below the plane of its ring. The applied magnetic field induces a large diamagnetic circulating current in the plane of the aromatic ring [14,15]. The secondary magnetic field due to this ring current then opposes the applied field at a point above or below the plane of the aromatic ring but de-shields the protons that lie along the axis, i.e., (XX'), of the ring.
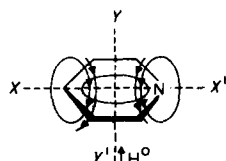
If it is now assumed that the protons of the $-CH_3$ substituent of β-picoline in pyridine (j) $+\beta$-picoline (i) mixtures align themselves along the six-fold axis of pyridine, i.e., lie along YY', then the chemical shift of the $-CH_3$ protons of β-picoline in pyridine would be shifted towards higher magnetic fields.

On the other hand, if the protons of methylenebromide in methylene-bromide (i) $+\beta$-picoline (j) lie along the XX' axis of β-picoline, then the chemical shift of the methylenebromide protons would be shifted towards low magnetic fields. The proton magnetic resonance studies of β-picoline (i)
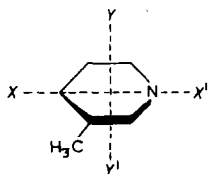
$+$ pyridine (j) and methylenebromide (i) $+\beta$-picoline (j) mixtures then suggests that β-picoline interacts with pyridine as
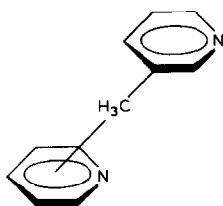
and methylenebromide interacts with β-picoline as

or
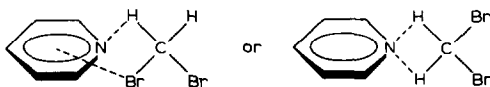
NMR studies on β-picoline (i) $+$ pyridine (j) and methylenebromide (i) $+\beta$-picoline (j) mixture thus show that whereas the β-picoline (i) $+$ pyridine (j) mixture is characterized by molecular interactions, that involve their C–C skelton, the methylenebromide (i) $+\beta$-picoline (j) mixture is characterized by specific interactions (i.e., involves not only their C–C skeletal interactions but also the valency of individual atoms) between the components of the mixture. This lends additional support to the qualitative information obtained from an analysis of their H_{ij}^E data in terms of the graph theoretical approach.

The results of the proton chemical shift of methylenebromide in β-picoline were then utilized to obtain a rough measurement of the distance of methylene-bromide protons from the plane of the aromatic ring in these molecular complexes by a method described elsewhere [16]. It was observed

that the average distance of methylenebromide protons from the XX' axis in the plane of β-picoline is 2.94 Å. If the hydrogen atom of methylenebromide lies perpendicularly to the N-atom of β-picoline in the plane of β-picoline, then the N–H distance becomes 2.54 Å. This N–H distance is slightly less
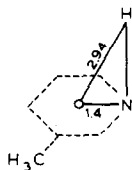
than the normal hydrogen bond length of 2.7 Å. Perhaps one of the bromine atoms of methylenebromide is also involved in accommodating the π-cloud of the aromatic ring in β-picoline in its vacant $3d$ orbitals, thereby shortening the N–H distance.

The proton chemical shift data of methylenebromide in methylenebromide (i) $+\beta$-picoline (j) mixtures were next utilized to evaluate the equilibrium constant of the following equilibria

$$\text{methylenebromide}(i) + \beta\text{-picoline}(j) \rightleftharpoons i : j$$
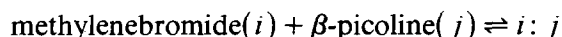
by a method described earlier [17]. The K value for this equilibrium was found to be 1.3 (on the mole fraction scale).

ACKNOWLEDGEMENT

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