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Note

Thermodynamic properties of α-picoline with aromatic hydrocarbons
1. Excess enthalpy of mixing

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A number of workers[1-3] have interpreted their excess enthalpy data on pyridine (A) + benzene (B) mixture in terms of specific interactions between its components. Murrell and Gil[4], from their n.m.r. studies, have even inferred the possible geometry of the complex. More recently Morcom et al.[5] have interpreted their H^E data of this mixture to suggest that pyridine is partly associated and that the mixture contains at least at 288.15 K, an AB_2 complex. As pyridine is both a π and n electron donor, it would be instructive to establish whether these interactions are predominantly π–π or n–π in character. The objectives of the present investigation is to understand these interactions and how they are modified when pyridine is replaced by α-picoline in its binary mixtures with the various aromatic hydrocarbons.

EXPERIMENTAL

Benzene, toluene, *o*-xylene, pyridine and α-picoline were purified and their purities checked as reported earlier[6,7].

Excess enthalpies were measured in an adiabatic calorimeter described earlier[8].

RESULTS

The excess enthalpies, H^E, are recorded in Table 1. The data were fitted to the expression

$$H^E/x_1(1-x_1)\ \mathrm{J\ mol^{-1}} = [h_0+h_1(2x_1-1)+h_2(2x_1-1)^2] \tag{1}$$

where x is the mole fraction of component. The parameters h_0, h_1, and h_2 evaluated by fitting $H^E/x_1(1-x_1)$ to expression 1 by the method of least squares, are given together with the standard deviations, $\sigma(H^E)$, in Table 2.

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TABLE 1

MEASURED HEATS OF MIXING AT DIFFERENT MOLE FRACTIONS x_1 OF COMPONENT 1 AT 308.15K

x_1	H^E ($J\ mol^{-1}$)	x_1	H^E ($J\ mol^{-1}$)
Pyridine + toluene			
0.1100	142.68	0.5470	216.24
0.1558	178.84	0.5891	202.98
0.2472	225.12	0.6100	196.88
0.3380	239.87	0.6315	190.84
0.3445	240.78	0.7204	158.12
0.4364	238.08	0.7562	143.62
0.4897	229.72	0.8011	124.18
Pyridine + o-xylene			
0.0968	184.01	0.5330	500.93
0.1324	245.14	0.5664	487.22
0.2163	365.05	0.6155	454.89
0.2540	405.12	0.6893	391.17
0.3104	455.98	0.7214	361.17
0.3822	500.20	0.7500	327.91
0.4096	509.10	0.8167	245.15
0.4334	512.90		
α-Picoline + benzene			
0.1368	47.25	0.5301	117.65
0.1737	58.94	0.5628	117.25
0.2250	72.70	0.5918	116.83
0.3342	99.25	0.6207	114.05
0.3631	104.99	0.6886	105.85
0.4146	111.28	0.7412	94.74
0.4561	114.92	0.8576	61.82
α-Picoline + o-xylene			
0.1252	85.42	0.5316	212.12
0.1876	122.95	0.5822	208.75
0.2362	146.89	0.6667	191.64
0.2875	167.18	0.7112	174.12
0.3168	182.20	0.7496	157.50
0.3439	190.69	0.8068	129.70
0.4610	211.87	0.8268	116.95
0.4743	212.80		

TABLE 2

VALUES OF PARAMETERS OF EQN (1) TOGETHER WITH THE VALUES OF STANDARD DEVIATIONS $\sigma(H^E)$ AT 308.15K

Mixture	*A*	*B*	*C*	$\sigma(H^E)$ ($J\ mol^{-1}$)
Pyridine + toluene	904.02	−420.15	350.08	0.93
Pyridine + *o*-xylene	2040.81	−400.12	−380.98	1.37
α-Picoline + benzene	469.84	71.67	−44.94	0.71
α-Picoline + *o*-xylene	855.80	20.07	−100.50	0.98

DISCUSSION

The heats of mixing pyridine and α-picoline with the various hydrocarbons are all endothermic, endothermicity varying in a manner consistent with the increased inductive effect of $-CH_3$ substitution in benzene. However, whereas the curve of H^E against the mole fraction x_1 of α-picoline is almost symmetrical about x_1 in its binary mixtures with benzene and *o*-xylene, the same is not true of the pyridine + toluene and pyridine + *o*-xylene mixtures; the maxima in the latter mixtures is skewed towards the aromatic hydrocarbon rich end of the mole fraction scale. There is, however, a considerable endothermic mixing in α-picoline + benzene and pyridine + *o*-xylene mixtures as compared to that of pyridine + benzene and α-picoline + *o*-xylene mixtures. This evidently speaks of some change in the nature of predominant interactions between the components of these mixtures. We now examine Murrell and Gil's[4] structure of the 1:1 pyridine–benzene complex in the light of our H^E data.

Murrell and Gil[4] have interpreted their n.m.r. data on pyridine + benzene mixture to suggest that pyridine forms a 1:1 complex with benzene; the benzene and pyridine molecules lying in parallel planes with the N atom of pyridine directly below one of the benzene H atom and the large dispersion energy of this structure of the complex is almost compensated by an electrostatic interaction between the negatively charged N atom and the C–H bond dipole of benzene. Subsequent addition of $-CH_3$ substituents to benzene as in the toluene and *o*-xylene would increase the predominant π–π interactions significantly as compared to the electrostatic interactions. Such a conjecture would, thus, envisage large endothermic mixing in pyridine + *o*-xylene mixture as compared to that in pyridine + toluene mixture. The experimental H^E data of these mixtures support this prediction. It would now be instructive to understand as to how these interactions are modified in the binary mixtures of α-picoline with benzene and *o*-xylene.

Assuming that these binary mixtures have the same type of interactions, as characterize the pyridine + benzene mixture, introduction of a $-CH_3$ substituent in pyridine would increase the π electron density in α-picoline. This would substantially increase the predominant π–π interaction without greatly influencing the electrostatic interactions in these mixtures. Such a scheme of the nature of interactions does explain the variation of endothermicity observed in these mixtures but cannot explain the much larger endothermic mixing in pyridine + *o*-xylene mixture as compared to that in α-picoline + *o*-xylene mixture. This could well be explained by assuming that the introduction of a $-CH_3$ substituent in pyridine displaces the π electron cloud towards its N atom rendering it more negative. This displacement of the π electron cloud in picolines has been shown[9] to be consistent with their interactions with chloroform. Consequently in α-picoline + benzene mixture there is an increase in both the predominant π–π and the electrostatic interactions, the increase in the former being considerable as compared to that of the latter. This would mean greater endothermic mixing in α-picoline + benzene mixture as compared to that in pyridine + benzene mixture. The experimental H^E data support this predication. Subsequent introduction of $-CH_3$ substituents to benzene as in *o*-xylene would substantially increase the π–π and electrostatic interactions in its binary mixtures with α-picoline as compared to that with pyridine. This would explain the much larger endothermic mixing in pyridine + *o*-xylene mixture as compared to that in α-picoline + *o*-xylene mixture.

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