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THERMODYNAMIC PROPERTIES OF BINARY MIXTURES OF α-PICOLINE AND ISO-ALIPHATIC ALCOHOLS

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The relationships enthalpy of mixing and excess Gibbs energy *vs.* composition were studied. We report here H^E and G^E for 2–CH_3–c–C_5H_4N (α-picoline) +

$(1-x)$ $CH_3CH(OH)CH_3$, $(1-x)$ $CH_3CHCH_3CH_2OH$,

$(1-x)$ $CH_3CH_2(OH)CHCH_3$ or $(1-x)$ $CH_3C(CH_3)(OH)CH_3$

Experimental

All the iso-alcohols used in the present paper were the same as those used in our previous study [1]. The apparatus and method used for measurement of H^E and G^E have already been described [2].

Results and discussion

The experimental results for H^E and G^E are summarized in Tables 1 and 2. Each set of results was fitted to the polynomial:

$$Y^E[\text{J mole}^{-1}] = x(1-x)\sum_{i=1}^{4} C_i x^{\frac{i-1}{2}} \qquad (1)$$

where Y^E is H^E or G^E.

The coefficients C_i and the standard deviations determined by the method of least squares, with all points weighted equally, are given in Table 3. G^E values are negative for all mixtures. The excess molar enthalpies are negative except for α-picoline + tert-butanol. The picolines retain all the characteristic properties of pyridine. They exhibit a free electron pair on the nitrogen atom and the asymmetric distribution of the π-electron density on the six atoms of the pyridine ring has been demonstrated by Wholand an Pauling:

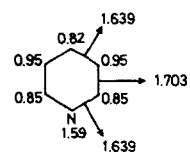

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Table 1 Excess enthalpies H^E of mixtures containing mole fraction x_p of α-picoline

x_p	$-H^E$, Jmole^{-1}	x_p	$-H^E$, Jmole^{-1}	x_p	$-H^E$, Jmole^{-1}	x_p	$-H^E$, Jmole^{-1}
$T = 293.15$ K							
α-picoline + 2-propanol				α-picoline + 2-butanol			
0.1070	66.51	0.4784	125.08	0.0823	38.75	0.4725	68.60
0.1977	117.81	0.4851	128.94	0.0923	44.56	0.4837	61.64
0.2626	123.39	0.5721	116.23	0.1050	50.75	0.6158	56.77
0.3017	123.66	0.6445	99.26	0.2000	62.70	0.6259	55.32
0.3611	128.05	0.7094	82.08	0.2344	65.31	0.7043	39.57
0.3637	129.92	0.7820	63.25	0.3040	69.59	0.7314	38.07
0.4368	132.86	0.9003	32.32	0.4200	70.50	0.8823	13.41
α-picoline + iso-butanol				α-picoline + tert-butanol $T = 313.15$ K			
0.1225	259.47	0.5722	439.66	0.0930	182.30	0.5782	54.59
0.1368	278.51	0.6712	405.98	0.1077	202.39	0.5027	91.42
0.2157	349.98	0.7008	359.94	0.2107	244.37	0.6286	0.0
0.3214	419.22	0.7212	381.77	0.2959	222.63	0.7076	+ 24.90
0.4125	441.03	0.7901	315.83	0.3229	202.37	0.7764	+ 27.28
0.4316	442.90	0.8006	293.89	0.4022	151.72	0.8085	+ 27.58
0.4408	452.27	0.8224	268.77	0.8376	+ 30.69	0.8993	+ 22.42
$T = 303.15$ K							
α-picoline + 2-propanol				α-picoline + 2-butanol			
0.0859	66.01	0.4114	112.07	0.0842	72.29	0.4366	110.86
0.0945	69.05	0.4495	103.05	0.1079	94.96	0.4630	109.23
0.0965	71.60	0.5175	98.54	0.1488	103.17	0.4863	104.62
0.1747	101.63	0.5330	97.51	0.1903	113.87	0.5662	93.64
0.2618	104.25	0.6494	79.20	0.2097	115.18	0.6370	77.61
0.2722	112.10	0.7507	66.69	0.2996	130.17	0.7312	60.05
0.2736	112.09	0.7746	51.94	0.3961	121.10	0.8079	47.45
α-picoline + iso-butanol $T = 303.15$ K				α-picoline + tert-butanol $T = 323.15$ K			
0.1044	200.64	0.5342	437.85	0.1086	148.72	0.5047	179.07
0.1909	313.58	0.5774	428.60	0.1118	180.10	0.5505	150.65
0.2388	372.93	0.5949	418.18	0.1207	182.18	0.6106	120.85
0.2875	399.30	0.6161	415.04	0.2168	309.61	0.6933	89.97
0.3577	426.52	0.6845	397.37	0.2771	316.25	0.7480	63.33
0.4102	431.12	0.7485	299.82	0.4437	227.85	0.8955	33.20
0.4798	447.53	0.8766	142.97	0.4766	190.77	0.9516	14.99

Table 2 Vapour pressures p, vapour-phase composition y, and liquid-phase composition x for binary mixtures at 323.15 K (x, y = mole fractions of α-picoline)

x_p	y_p	$-G^E$, Jmole^{-1}	p, Torr	x_p	y_p	$-G^E$, Jmole^{-1}	p, Torr
α-picoline + 2-propanol				α-picoline + 2-butanol			
1.0	1.0	–	5.55	1.0	1.0	–	5.55
0.9550	0.8000	173.65	6.13	0.9650	0.9510	10.10	5.67
0.9351	0.7501	135.67	6.49	0.9480	0.9251	16.85	5.72
0.9001	0.6452	203.81	7.03	0.9220	0.8702	53.20	5.80
0.8650	0.5702	206.43	7.61	0.8750	0.8151	90.36	5.89
0.7754	0.4303	215.59	9.12	0.7981	0.6903	149.20	6.15
0.6802	0.3000	215.03	10.90	0.7482	0.6351	170.60	6.38
0.6306	0.2604	218.11	11.73	0.6956	0.5482	185.15	6.58
0.5950	0.2150	216.18	12.68	0.5304	0.3503	259.81	7.27
0.4802	0.1611	185.01	14.40	0.5045	0.3102	243.75	7.54
0.4083	0.1301	145.11	15.57	0.4083	0.2551	225.34	7.95
0.3001	0.0802	114.46	17.47	0.3052	0.1651	179.53	8.58
0.2405	0.0600	90.44	18.53	0.2421	0.1152	166.98	9.00
0.1954	0.0451	84.49	19.34	0.2006	0.1003	124.99	9.22
0.0800	0.0151	48.01	21.07	0.1903	0.0851	113.95	9.41
0.0	0.0	–	23.08	0.1381	0.0622	90.64	9.70
				0.0	0.0	–	10.70
α-picoline + iso-butanol				α-picoline + tert-butanol			
1.0	1.0	–	5.55	1.0	1.0	–	5.55
0.9303	0.9401	66.97	5.54	0.9105	0.7701	118.38	6.40
0.7800	0.7902	150.18	5.53	0.8352	0.6000	146.24	7.59
0.7402	0.7301	199.89	5.54	0.7750	0.5211	160.45	8.30
0.6551	0.6351	250.08	5.55	0.7101	0.4004	184.11	9.37
0.6484	0.6250	254.95	5.57	0.6501	0.3101	199.20	10.94
0.5401	0.4951	292.31	5.67	0.6154	0.3152	206.64	11.58
0.4252	0.3605	305.06	5.84	0.5485	0.2411	213.79	12.67
0.3661	0.2800	296.35	6.00	0.4904	0.2001	223.69	13.74
0.3006	0.2082	276.82	6.19	0.4153	0.1383	218.19	14.94
0.2275	0.1503	224.49	6.42	0.3651	0.1112	207.49	16.36
0.1725	0.0981	206.08	6.50	0.2903	0.1200	140.98	18.00
0.1613	0.0951	179.88	6.66	0.2254	0.0500	175.23	18.97
0.1203	0.0624	149.58	6.85	0.1803	0.0451	157.74	20.00
0.0521	0.0211	82.94	7.07	0.1202	0.0211	129.75	21.29
0.0	0.0	–	7.28	0.0	0.0	–	23.33

Table 3 Coefficients of Eq. (i) for binary mixtures, with the corresponding standard deviation $\delta(Y^E)$ [Jmole^{-1}]

Mixtures	Y^E	T, K	C_1	C_2	C_3	C_4	$\delta(Y^E)$, Jmole^{-1}
α-picoline +	H^E	293.15	−499.00	253.10	−77.84	8.49	4.29
2-propanol	H^E	303.15	−402.68	194.87	−209.44	237.67	3.43
	G^E	323.15	672.92	807.85	1066.54	–	28.92
α-picoline +	H^E	293.15	−258.48	119.20	−70.96	215.67	2.62
2-butanol	H^E	303.15	−412.57	319.88	−287.67	131.63	3.79
	G^E	323.15	984.77	53.66	−453.87	–	1.06
α-picoline +	H^E	293.15	−1778.75	226.33	−729.88	195.11	17.30
iso-butanol	H^E	303.15	−1780.18	165.61	124.11	620.95	8.27
	G^E	323.15	1197.85	−3268.8	−84.80	–	9.76
α-picoline +	H^E	313.15	−344.79	1375.54	−885.36	194.54	8.26
tert-butanol	H^E	323.15	−785.48	1572.81	−612.50	−1120.37	18.0
	G^E	323.15	837.05	25.53	492.03	–	18.2

It is evident that the π-electron concentration is highest on the nitrogen. In the picolines as compared with pyridine, the asymmetry of the charge distribution is even greater, because of the inductive effect of the $-CH_3$ substituent, this enhancing their electronegative nature. The occurrence of intermolecular bonds in α-picoline is therefore very probable [3]. The polarity of the α-picoline molecule is greater than that of β-picoline. It is well known that alcohols form associations. In this case the steric effect strongly influences hydrogen-bond formation. As concerns the investigated iso-aliphatic alcohols the steric effect is greatest for tert-butyl alcohol (owing the presence of three sterically large methyl groups). The alcohols studied assumed the following sequence of increasing steric effect:

iso-butanol < 2-propanol < 2-butanol < tert-butanol.

The formation of hydrogen-bonds is smallest for tert-butanol, and greatest for iso-butanol, which is confirmed by the boiling temperatures of the investigated alcohols, which decrease in the sequence iso-butanol > 2-butanol > tert-butanol. In the mixtures of α-picoline with the above four iso-aliphatic alcohols, the G^E values (which are always negative) increase in the sequence tert-butanol < 2-propanol < 2-butanol < < iso-butanol. The fact that the G^E values are always negative points to the predominance of formation of new bonds between molecules of different compounds, as compared with the breaking of bonds between molecules of the same compound.

Due to the strongly polar nature of both components of the mixtures, the induction and orientation effects may greatly influence the intermolecular interactions. The entropy effect resulting from the difference in molecular size between the components of the mixtures can also influence the behaviour of functions G^E and H^E.

The present results are only qualitative. Quantitative interpretation presents difficulties, caused by the complex nature of the mixtures and by the superposition of various intermolecular interactions [4].

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Zusammenfassung – Die Beziehungen Zwischen Mischungsenthalpie und Gibbs'scher Überschußenergie und der Zusammensetzung werden untersucht. H^E und G^E werden für die Systeme 2–CH_3–c–C_5H_4N (α-Picolin) +

$(1-x)\ CH_3CH(OH)CH_3$, $(1-x)\ CH_3CHCH_3CH_2OH$,

$(1-x)\ CH_3CH_2(OH)CHCH_3$ oder $(1-x)\ CH_3C(CH_3)(OH)CH_3$

Резюме – Изучена взаимосвязь между энтальпией смешения, избыточной энергией Гиббса и составом смеси. Приведены значения H^E и G^E для смесей α-пиколин +

$(1-x)\ CH_3CHOHCH_3$, $(1-x)\ (CH_3)_2CHCH_2OH$,

$(1-x)\ CH_3CH_2CHOHCH_3$, $(1-x)\ CH_3C(CH_3)(OH)CH_3$.