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EXCESS ENTHALPIES IN PYRIDINE BASE-METHANOL SYSTEMS

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The excess enthalpy of mixing versus composition was studied at 293.15 K and 303.15 K for some binary mixtures of methanol with pyridine bases. The results are presented in Tables.

The main purpose of this paper is to report on the molar excess heats of mixing for: methanol + α-picoline, methanol + β-picoline, methanol + γ-picoline, methanol + 2,4-lutidine, methanol + 2,6-lutidine, and methanol + 2,4,6-collidine at 293.15 and 303.15 K. The influences of the basicity of the pyridine base and its structure on the excess functions studied are evaluated by comparing the results in the present mixtures with those for methanol + α-, β- or γ-picoline, 2,4-lutidine, 2,6-lutidine, 2,4,6-collidine.

Experimental

The alcohol was purified as suggested by Weissberger [1]. All pyridine bases were dried over potassium hydroxide and purified by fractional distillation. The purity of the final samples was checked by measuring their densities and with an analytical gaschromatograph using a column containing alkalinified 10 per cent Carbowax 1000 on GCHQ 80/100 mesh. The purity was estimated to be 99.9 mole per cent. Excess enthalpies were measured at 293.15 and 303.15 K, using the calorimetric method described previously [2]. The accuracy of the H^E results is estimated to be better than ±1.5 per cent over most of the concentration range.

Results

Measurements were made over the whole concentration range. The thermodynamic molar excess heats of mixing for six binary systems at various compositions are given in Tables 1 and 2. The values of the excess functions were fitted to an equation of the form:

$$H^E = x(1 - x) \sum_{i=1}^{k} C_i(2x - 1)^{i-1} \quad (1)$$

where H^E represents the excess enthalpies and x_A is the mole fraction of alcohol. The adjustable coefficients C_i calculated by the method of least squares are given in Table 3, together with the standard deviations [3] $\sigma(H^E)$ of the results: the standard error is defined by

Table 1

Excess enthalpies H^E of mixtures containing mole fraction x_A of alcohol

T, K	x_A	$-H^E$, J mole^{-1}	x_A	$-H^E$, J mole^{-1}	x_A	$-H^E$ J mole^{-1}	x_A	σH^E, J mole^{-1}
293.15	*Methanol + α-picoline*			*Methanol + β-picoline*				
	0.0916	298.15	0.6154	1242.91	0.1329	21.00	0.4791	116.34
	0.2015	643.27	0.6575	1189.24	0.1997	40.09	0.5657	133.90
	0.3025	862.03	0.7004	1115.99	0.2512	57.59	0.6087	138.11
	0.4611	1167.27	0.7550	1004.32	0.3402	79.81	0.6172	143.21
	0.5037	1228.14	0.8112	896.11	0.3752	80.56	0.7520	116.52
	0.5502	1272.31	0.9004	577.21	0.4302	97.99	0.8740	71.97
293.15	*Methanol + γ-picoline*			*Methanol + 2,4-lutidine*				
	0.1174	182.00	0.6008	811.35	0.0688	212.82	0.5247	1286.30
	0.2037	345.93	0.6502	793.23	0.1045	414.65	0.6321	1197.71
	0.3004	471.32	0.7003	745.17	0.1655	665.20	0.7051	1203.80
	0.4138	640.33	0.7714	632.82	0.2161	870.39	0.7937	1146.30
	0.5050	773.29	0.8049	530.49	0.2961	1054.87	0.8406	967.25
	0.5538	806.15	0.9005	310.72	0.3401	1135.49	0.9053	697.29
					0.4060	1213.21	0.9528	269.55
					0.4829	1265.53		
293.15	*Methanol + 2,6-lutidine*			*Methanol + 2,4,6-collidine*				
	0.0341	214.11	0.5758	1137.29	0.1457	385.42	0.5389	850.37
	0.1307	718.32	0.6623	971.68	0.2381	561.99	0.5917	830.72
	0.1948	977.68	0.7234	853.78	0.3180	691.82	0.6518	796.44
	0.2956	1198.29	0.7708	612.29	0.3988	791.08	0.6909	764.28
	0.3948	1287.72	0.8063	518.13	0.4283	825.65	0.7899	696.98
	0.4722	1276.78	0.9106	253.58	0.4967	849.44	0.8707	425.69

$$\sigma = [(\sum H^E_{exp} - H^E_{calc})^2 (n - k)^{-1}]^{1/2} \quad (2)$$

where k is the number of coefficients needed to represent the results adequately and the sum is taken over the set of n results.

Discussion

The values of the excess enthalpies in all mixtures investigated are negative. The H^E values for concentrated mixtures at both temperatures increase in the sequence: 2,4,6-collidine < 2,6-lutidine < 2,4-lutidine < α-picoline < β-picoline < γ-picoline, when the other component is methanol.

When the temperature increases, the H^E values for mixtures of methanol +α-, β- or γ-picoline, 2,4- or 2,6-lutidine or 2,4,6-collidine increase, too. The basicity of pyridine and its methyl derivatives, expressed by K_a, increases in the order [4] pyridine < β-picoline < α-picoline < γ-picoline < 2,6-lutidine < 2,4-luti-

Table 2

Excess enthalpies H^E of mixtures containing mole fraction x_A of alcohol

T, K	x_A	$-H^E$, J mole^{-1}	x_A	$-H^E$, J mole^{-1}	x_A	$-H^E$, J mole^{-1}	x_A	$-H^E$, J mole^{-1}
303.15	*Methanol + α-picoline*				*Methanol + β-picoline*			
	0.1015	282.42	0.5500	1061.71	0.0998	125.08	0.5233	853.90
	0.2014	536.52	0.5985	1069.12	0.1411	298.05	0.6315	861.13
	0.3024	757.01	0.6988	950.99	0.2656	341.65	0.6990	830.11
	0.3562	842.15	0.7550	870.92	0.3393	493.04	0.7493	756.07
	0.4104	918.59	0.8111	777.51	0.3771	584.29	0.8501	512.95
	0.5013	1023.09	0.9004	475.37	0.4699	769.88	0.8817	415.82
303.15	*Methanol + γ-picoline*				*Methanol + 2,4-lutidine*			
	0.1175	141.94	0.6017	696.49	0.0671	374.47	0.5002	1167.36
	0.1988	279.54	0.6529	681.90	0.0901	446.68	0.5266	1202.64
	0.3002	441.62	0.7042	643.01	0.1348	573.74	0.6072	1200.42
	0.4134	616.73	0.7524	549.83	0.1833	687.16	0.6418	1189.68
	0.5050	687.70	0.8039	445.23	0.2385	792.51	0.7283	1064.59
	0.5531	697.92	0.9003	228.17	0.3179	950.66	0.8909	642.39
					0.4241	1096.1	0.9612	370.46
303.15	*Methanol + 2,6-lutidine*				*Methanol + 2,4,6-collidine*			
	0.1001	510.24	0.4936	1152.27	0.0913	525.33	0.5697	1540.15
	0.2027	855.18	0.5886	1057.79	0.1480	771.65	0.6177	1500.19
	0.3034	1080.46	0.6666	951.26	0.2100	950.77	0.6991	1349.66
	0.3467	1148.35	0.7704	708.63	0.2763	1249.23	0.7468	1275.02
	0.4026	1177.00	0.8002	633.82	0.4056	1484.83	0.7972	1113.88
					0.5000	1570.63	0.8802	750.33

dine < 2,4,6-collidine. This order does not agree with that for the H^E values in the mixtures of pyridine bases and methanol. For small differences in K_a values, e.g. for α- and γ-picoline, significant differences in the H^E values of their mixtures with methanol were observed. This shows that not only the basicity of the pyridine bases influence the H^E values.

The differences in structure of the basic components are evident and the H^E values of their mixtures with methanol are dependent on the number and positions of the methyl groups in the pyridine base molecule. The results obtained show that the methyl group contributions to the H^E values, are always negative. Methyl groups in positions 2 and 6 have the most important influence on the value of H^E. All our results confirm earlier suggestions [5, 6] of self-association (dimerization) of molecules of the pyridine bases containing at least one hydrogen atom bonded to the carbon atom which is the nearest neighbour of the nitrogen atom. It is assumed that these data and [7] are important proofs of the hypothesis of the self-association of some pyridine bases.

Table 3

Coefficients of equation (1) for the investigated mixtures, and standard deviation (J mole^{-1})

Mixtures: methanol +	T,K	C_1	C_2	C_3	C_4	$\sigma(H^E)$, (J mole^{-1})
α-picoline	293.15	− 4794.2	− 1611.3	− 245.5	528.1	1.83
	303.15	− 4988.4	− 1580.4	309.8	499.9	3.10
β-picoline	293.15	− 3678.2	− 1705.3	306.2	627.6	0.99
	303.15	− 3120.3	− 1698.9	306.8	748.5	0.89
γ-picoline	293.15	− 3044.9	− 1584.9	− 1720.1	684.9	1.01
	303.15	− 2337.7	− 975.2	311.1	423.7	0.96
2,4-lutidine	293.15	− 5422.7	− 1590.4	− 397.8	748.3	1.86
	303.15	− 4357.0	1501.1	355.9	− 621.0	2.07
2,6-lutidine	293.15	− 5015.2	− 1987.7	− 520.1	− 435.6	3.02
	303.15	− 4635.9	− 1205.9	− 734.6	− 999.8	6.16
2,4,6-collidine	293.15	− 5748.3	− 209.8	− 2269.9	− 800.9	1.95
	303.15	− 6423.4	− 459.3	− 704.9	− 222.7	4.09

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RÉSUMMÉ — La variation de l'enthalpie de mélange en fonction de la composition a été étudiée à 293.15 K et 303.15 K dans quelques mélanges binaires de méthanol et de pyridine base. Les résultats sont présentés sous forme de tableaux.

ZUSAMMENFASSUNG — Der Zusammenhang zwischen Mischungsenthalpie und Zusammensetzung wurde bei 293.15 K und 303.15 K an einigen Binärsystemen von Methanol mit Pyridinbasen untersucht. Die Ergebnisse werden in Tabellen aufgeführt.

Резюме — Исследованы энтальпии смешения нескольких бинарных смесей метанола с пиридиновыми основаниями в зависимости от состава при температурах 293.15 К и 303,15 К. Результаты исследований приведены в таблицах.