Journal of Thermal Analysis, Vol. 29 (1984) 173–177

MOLAR EXCESS ENTHALPIES OF BINARY MIXTURES OF PYRIDINE BASES + HEXAN-1-OL

T. Kasprzycka-Guttman, A. Myślińnski and *H. Wilczura*

DEPARTMENT OF CHEMICAL TECHNOLOGY, WARSAW UNIVERSITY,
02-093 WARSAW, PASTEURA 1, POLAND

(Received July 19, 1983)

The excess enthalpies at 303.15 K of binary mixtures of hexan-1-ol + pyridine, α-, β- and γ-picolines, 2,4- and 2,6-lutidines and 2,4,6-collidine have been measured as a function of composition.

Experimental

After preliminary drying over KOH, the pyridine bases (p.a.) were rectified through a rectifying column and fractions boiling within ±0.02° were collected. Hexan-1-ol (p.a.) was dried over calcined anhydrous sulphates and rectified. The degrees of purity of the pyridine bases and the alcohol were determined by density measurements and by gas chromatography. The purity of the pyridin bases was estimated to be 99.9 mole percent, and that of the alcohol 98.99 percent. Excess enthalpies were measured using the calorimetric method described previously [1].

The calorimeter was checked by determination of the excess enthalpy of the benzene + cyclohexane system at 303.15 K. Our results were consistent with the data from the literature within approx. 1.0 percent [2–4].

Results

Measurements of the excess enthalpy H^E were made *vs.* the mole fraction of the alcohol. The excess enthalpies for seven binary systems, at various compositions, are given in Fig. 1.

The measured values were correlated through the equation:

$$H^E = x(1-x)\sum_{i=1}^{3} C_n(2x-1)^{i-1} \tag{1}$$

where H^E is the excess enthalpy and x is the mole fraction of hexan-1-ol.

The adjustable coefficients C_n, calculated by the method of least squares, are collected in Table 1, together with the standard deviations $\delta(H^E)$ of the results for H^E.

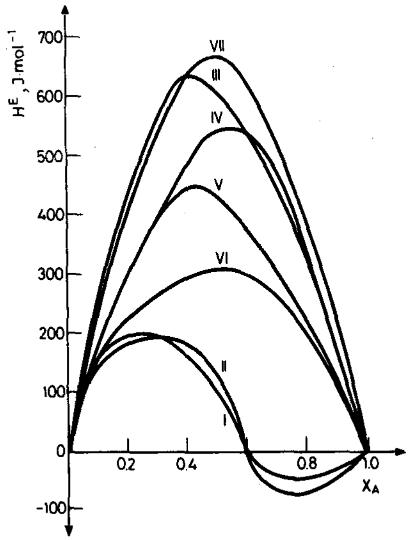

Fig. 1 Excess enthalpies of mixing H^E vs. x_A for binary systems: I. hexan-1-ol + γ-picoline; II. hexan-1-ol + β-picoline; III. hexan-1-ol + 2,4,6-collidine; IV. hexan-1-ol + 2,4-lutidine; V. hexan-1-ol + 2,6-lutidine; VI. hexan-1-ol + α-picoline; VII. hexan-1-ol + pyridine at 303.15 K

Table 1 Coefficients of Redlich–Kister equation (1) and standard deviations $\delta(H^E)$

Mixtures: hexanol +	T, K	C_1	C_2	C_3	$\delta(H^E)$, J mole^{-1}
pyridine	303.15	− 2992.46	− 307.95	518.21	0.98
α-picoline	303.15	− 1027.26	− 480.61	195.82	0.00
β-picoline	303.15	249.11	− 747.86	− 427.11	2.5
γ-picoline	303.15	− 2.19	314.48	− 2.14	3.02
2,4-lutidine	303.15	− 2088.48	− 478.38	− 388.41	2.99
2,6-lutidine	303.15	1691.44	508.21	− 545.03	4.7
2,4,6-collidine	303.15	1402.07	740.49	1517.44	2.9

The values of the excess enthalpies in the binary mixtures hexan-1-ol + pyridine, α-picoline, 2,4-lutidine, 2,6-lutidine and 2,4,6-collidine are negative, but hexan-1-ol + + β-picoline and γ-picoline give S-shaped curves at 303.15 K.

The H^E values vary in the sequence: 2,4,6-collidine < 2,4-lutidine < pyridine < < α-picoline < β-picoline < γ-picoline. The differences in structure of the basic components are evident and the H^E values of their mixtures with hexan-1-ol and other aliphatic alcohols are dependent on the number and positions of the methyl groups in the pyridine base molecules. Methyl groups in positions 2 and 6 have an important influence on the value of H^E. This was noted by Kiefer, Becker [5] and Cox [6] and was confirmed in our work.

The physicochemical properties of normal aliphatic alcohol molecules are determined by the presence of a hydroxy group and by the number of carbon atoms in the molecule. It is generally accepted that the OH group is mostly responsible for the structural properties. This group allows for the formation of $(R{-}OH)_x$ associates through H-bonding. Various investigations indicate that the x values lie within the limits 2–5. Most frequently, a value of 3 is given as the most probable for low molecular mass representatives.

The values of the OH groups in the alcohols considered in our work may be regarded as constant [6].

It may be stated that the increase in the excess volumes of the individual alcohols is caused by an increase in the hydrocarbon chain of the molecule. If the excess volume values of the $=CH_2$ groups at 298.15 K for normal aliphatic alcohols are listed, it may observed that for $C_3{-}C_7$ the participations of particular $=CH_2$ groups are constant. Individual results differ by less than one per cent from the mean value, which equals 16.648 cm^3 per mole [7].

At the same time, the presence and position of CH_3 groups with regard to the nitrogen atom in a pyridine ring determines the change in the form and size of a given pyridine base molecule.

The measured volumes for pyridine bases at 298.15 K [7]:

$V_{\text{pyrid.}} = 80.872\ \text{cm}^3/\text{mol}$ $V_{2,4\text{-lut.}} = 115.614\ \text{cm}^3/\text{mol}$

$V_{\alpha\text{-pic.}} = 99.139\ \text{cm}^3/\text{mol}$ $V_{2,6\text{-lut.}} = 116.374\ \text{cm}^3/\text{mol}$

$V_{\beta\text{-pic.}} = 97.794\ \text{cm}^3/\text{mol}$ $V_{2,4,6\text{-col.}} = 133.127\ \text{cm}^3/\text{mol}$

$V_{\gamma\text{-pic.}} = 97.999\ \text{cm}^3/\text{mol}$

It may be observed that the molar participation of the first methyl group for various positions is as follows:

position α: $V_{\alpha\text{-CH}_3} = 18.267\ \text{cm}^3/\text{mol}$

position β: $V_{\beta\text{-CH}_3} = 16.922\ \text{cm}^3/\text{mol}$

position γ: $V_{\gamma\text{-CH}_3} = 17.127\ \text{cm}^3/\text{mol}$

Assuming the additiveness of the volume values of the methyl groups, the following values are obtained for lutidines and collidine:

$$V_{2,4\text{-lut.}} = V_{\text{pyr.}} + \Delta V_{\alpha\text{-CH}_3} + \Delta V_{\gamma\text{-CH}_3} = 116.266\ \text{cm}^3/\text{mol}$$

$$V_{2,6\text{-lut.}} = V_{\text{pyr.}} + 2\Delta V_{\alpha\text{-CH}_3} = 117.406\ \text{cm}^3/\text{mol}$$

$$V_{2,4,6\text{-col.}} = V_{\text{pyr.}} + 2\Delta V_{\alpha\text{-CH}_3} + \Delta V_{\gamma\text{-CH}_3} = 134.533\ \text{cm}^3/\text{mol}$$

Similarly, we can calculate the participation values of methyl groups in the α, β and γ positions in the molar excess enthalpy of mixing for a given composition and temperature:

Methyl group in position α:

$$nH^E_{x_2,\alpha\text{-pic.}} - nH^E_{x_2,\text{pyr.}} = n\Delta H^E_{x_2,\text{pyr.}} = n\Delta H^E_{x_2,\alpha\text{-CH}_3}$$

Methyl group in position β:

$$nH^E_{x_2,\beta\text{-pic.}} - nH^E_{x_2,\text{pyr.}} = n\Delta H^E_{x_2,\beta\text{-CH}_3}$$

Methyl group in position γ:

$$nH^E_{x_2,\gamma\text{-pic.}} - nH^E_{x_2,\text{pyr.}} = n\Delta H^E_{x_2,\gamma\text{-CH}_3}$$

With these formulae, the assumed H^E values for the given concentration values have been calculated for the mixtures of the remaining pyridine bases as follows:

Mixtures of 2,4-lutidine:

$$nH^E_{x_2,2,4\text{-lut.}} = nH^E_{x_2,\text{pyr.}} + n\Delta H^E_{x_2,\alpha\text{-CH}_3} + n\Delta H^E_{x_2,\gamma\text{-CH}_3}$$

Mixtures of 2,6-lutidine:

$$nH^E_{x_2,2,6\text{-lut.}} = nH^E_{x_2,\text{pyr.}} + 2n\Delta H^E_{x_2,\alpha\text{-CH}_3}$$

Mixtures of 2,4,6-collidine:

$$nH^E_{x_2,2,4,6\text{-col.}} = nH^E_{x_2,\text{pyr.}} + 2n\Delta H^E_{x_2,\alpha\text{-CH}_3} + n\Delta H^E_{x_2,\gamma\text{-CH}_3}$$

It appears that the results which are closest to the experimental values have been obtained for 2,6-lutidine and 2,4,6-collidine. The data presented point to a specific property of the methyl group in the α position. The deviation is smaller than 0.8 percent. The results of H^E and V^E measurements indicate that the biggest differences are caused by a methyl group or groups in the α and α' positions. Nevertheless, the final solution of this problem cannot be obtained by determining the values of excess functions and investigating the influence of methyl groups upon these functions. The special property of the methyl group in position α is one of the factors influencing the values of excess functions, apart from many other specific interactions.

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