Journal of Thermal Analysis, Vol. 14 (1978) 123—130

MOLAR EXCESS ENTHALPIES AND VOLUMES OF MIXTURES OF 2,4,6-TRIMETHYL-PYRIDINE WITH SOME ALIPHATIC ALCOHOLS

T. KASPRZYCKA-GUTTMAN, B. KOWALSKI and A. ORSZÁGH

Department of Chemical Technology, Warsaw University, 02093 Warszawa, Poland

(Received August 21, 1977)

The relationship enthalpy of mixing and excess molar volume of mixing versus composition were studied at 313.15 K for binary systems of 2,4,6-collidine with normal aliphatic alcohols. It was found that at this temperature the values of H^E and V^E are negative and change with the length of the alkyl group of the alcohol.

As a continuation of our studies on thermodynamic excess functions of mixing for mixtures containing pyridine bases and alcohols, we have used 2,4,6-trimethylpyridine and propan-1-ol, butan-1-ol, pentan-1-ol and hexan-1-ol. 2,4,6-Trimethylpyridine is the most basic ($pK_a = 7.5$ [1] of all the pyridine bases investigated by us so far. On the other hand, as suggested by Kiefer and Becker [2] and Cox [3], the presence of the methyl groups near the basic nitrogen means that specific self-association via hydrogen-bonds does not occur in this liquid. It may be expected that the H^E and V^E values for mixtures of 2,4,6-collidine + alcohols will be more negative compared with systems consisting of other pyridines and fixed alcohols. The purpose of the present work is to evaluate the influence of the basicity of the pyridine base and its structure on the excess functions studied, by comparing the results for the present mixtures with those for an alcohol + pyridine, α-, β- or γ-picoline, 2,4-lutidine or 2,6-lutidine.

Experimental

All alcohols were the same as those used previously [4, 5]. After purification 2,4,6-collidine was checked with an analytical gas-chromatograph. The purity was estimated to be 99.9 mole per cent. The H^E and V^E measurements were made at 313.15 K. Excess enthalpies were measured by direct mixing in a Dewar vessel, using the method and apparatus described previously [6]. The accuracy of the H^E results is estimated to be better than ± 1.5 per cent over most of the concentration range. Excess volumes were measured by the pycnometric technique. The precision of V^E is estimated to be about 0.004 cm^3 mole^{-1} for the equimolar mixtures.

Results

Experimental results for the excess molar enthalpies and the excess molar volumes of the present mixtures are summarized in Tables 1 and 2, respectively. The values of the excess functions were fitted to an equation of the form:

Table 1

Excess enthalpies H^E of mixtures containing mole fraction x of alcohol at 313.15 K

x	$-H^E$ J mole^{-1}	x	$-H^E$ J mole^{-1}	x	$-H^E$ J mole^{-1}	x	$-H^E$ J mole^{-1}
Propan-1-ol + 2,4,6-collidine				*Butan-1-ol + 2,4,6-collidine*			
0.1032	334.2	0.5278	890.1	0.0968	275.6	0.5000	809.0
0.1822	529.9	0.6025	843.4	0.1696	429.6	0.6014	718.5
0.2346	635.4	0.6582	772.6	0.2010	487.3	0.6680	659.6
0.3100	763.3	0.7091	693.9	0.2699	646.3	0.6943	610.9
0.3769	850.7	0.7964	515.4	0.3432	700.1	0.7985	412.5
0.4420	889.5	0.8885	301.9	0.4268	778.8	0.9068	198.9
Pentan-1-ol + 2,4,6-collidine				*Hexan-1-ol + 2,4,6-collidine*			
0.0897	241.8	0.4777	719.9	0.0889	202.3	0.4797	669.0
0.1804	400.3	0.5891	678.0	0.1580	342.3	0.5662	648.9
0.2515	514.3	0.6378	651.1	0.2069	428.6	0.6454	600.3
0.3079	615.5	0.7139	574.5	0.2719	510.8	0.7139	541.3
0.3995	690.2	0.7760	480.2	0.3457	597.4	0.8010	420.9
0.4519	718.0	0.8372	357.9	0.4040	636.5	0.8968	209.3

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

where Y^E represents either H^E or V^E and x 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 $\sigma(Y^E)$ of the results. We have found no previous results to compare with our results of H^E and V^E.

The excess enthalpies and the excess volumes for all systems represented are negative over the entire concentration range. The H^E and V^E values vary in the sequence: propan-1-ol < butan-1-ol < pentan-1-ol < hexan-1-ol in their mixtures with 2,4,6-collidine. This is similar to the pattern observed for other pyridine base + alcohol binary mixtures studied by us previously. The negative values of both functions suggest that the 2,4,6-collidine + alcohol mixtures involve a specific interaction via the N $\cdots$ H–O bond. The results show that the N $\cdots$ H–O bonding is stronger than the O $\cdots$ H–O bonding. Comparing both excess functions for binary mixtures consisting of pyridine bases with a fixed alcohol from propan-1-ol to hexan-1-ol, we found that H^E and V^E vary in sequences A and B, respectively. In the second line of sequence B the pK_a values are given. The pK_a values were taken from Perrin's compilation [1].

Sequence A : H^E :
2,4,6-collidine < 2,4-lutidine < 2,6-lutidine < α-picoline < < β-picoline < γ-picoline < pyridine.

Table 2

Excess volumes V^E of mixtures containing mole fraction x of alcohol at 313.15 K

x	$-V^E$, cm« mole^{-1}	x	$-V^E$, cm^3 mole^{-1}	x	$-V^E$, cm^3 mole^{-1}	x	$-V^E$, cm^3 mole^{-1}
Propan-1-ol + 2,4,6-collidine				*Butan-1-ol + 2,4,6-collidine*			
0.0504	0.182	0.5138	1.154	0.0493	0.183	0.5256	1.125
0.0995	0.341	0.5688	1.130	0.0982	0.337	0.5989	1.078
0.1509	0.497	0.5954	1.108	0.1500	0.487	0.6538	1.020
0.2002	0.630	0.6482	1.050	0.2237	0.689	0.6955	0.966
0.2492	0.759	0.6973	0.981	0.3003	0.870	0.7462	0.868
0.2999	0.880	0.7409	0.882	0.3412	0.952	0.7896	0.784
0.3477	0.983	0.7965	0.792	0.3888	1.040	0.8312	0.628
0.4012	1.073	0.8500	0.650	0.4651	1.120	0.8980	0.425
0.4489	1.128	0.9012	0.466	0.5011	1.132	0.9481	0.184
Pentan-1-ol + 2,4,6-collidine				*Hexan-1-ol + 2,4,6-collidine*			
0.0499	0.180	0.5441	1.103	0.0505	0.149	0.4972	1.096
0.1021	0.341	0.5688	1.130	0.1049	0.326	0.5517	1.078
0.2002	0.612	0.6421	1.005	0.1568	0.473	0.5943	1.030
0.2500	0.742	0.7071	0.934	0.2152	0.620	0.6447	0.988
0.2962	0.850	0.7477	0.850	0.2654	0.755	0.7003	0.912
0.3450	0.955	0.7998	0.730	0.2940	0.819	0.7312	0.849
0.3965	1.045	0.8448	0.602	0.3439	0.921	0.7819	0.731
0.4433	1.109	0.9009	0.410	0.3937	1.011	0.8508	0.541
0.4966	1.114	0.9518	0.182	0.4441	1.065	0.9263	0.256

Table 3

Coefficients C_i of the equation with the corresponding standard deviation (Y^E) J. mole^{-1} or cm^3.mole^{-1} at 313.15 K

Mixture	Y^E	C_1	C_2	C_3	C_4	$\sigma(Y^E)$
2,4,6-collidine	H^E	− 3577.3	214.7	536.7	241.0	5.9
+ propan-1-ol	V^E	− 4.577	− 0.478	0.965	− 0.618	0.014
2,4,6-collidine	H^E	− 3156.1	352.4	800.0	182.5	16.0
+ butan-1-ol	V^E	− 4.488	− 0.540	0.750	0.155	0.016
2,4,6-collidine	H^E	− 2863.3	45.6	240.4	− 23.4	12.1
+ pentan-1-ol	V^E	− 4.443	− 0.379	0.973	− 0.357	0.017
2,4,6-collidine	H^E	− 2667.3	− 70.3	286.7	262.3	8.9
+ hexan-1-ol	V^E	− 4.333	− 0.413	1.144	− 0.073	0.013

Sequence B : V^E:

2,4,6-collidine $<$ 2,6-lutidine $\ll$ α-picoline $\approx$
7.5 6.7 5.9
2,4-lutidine $\ll$ γ-picoline $\approx$ β-picoline $<$ pyridine
6.7 6.0 5.7 5.2

These orders show that not only the basicity of the pyridine bases influences the H^E and V^E values. The differences in structure of the basic components are evident and the thermodynamic excess properties of their mixtures with alcohols are generally dependent on the number and positions of the methyl groups in the pyridine base molecule. All results obtained show that the methyl group contributions to the H^E or V^E values are always negative. Especially for the V^E values the methyl groups in positions 2 and 6 have the most important influence. Thus, the specific influence of the α-CH_3 groups can be interpreted as a hindrance in self-association of some pyridine base molecules [2, 3].

References

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Résumé — La variation de l'enthalpie de mélange et du volume molaire d'excès en fonction de la composition a été étudiée à 313.15 K, dans des systèmes binaires de collidine 2,4,6 et d'alcools aliphatiques normaux. On a établi qu'à cette température les valeurs de H^E et de V^E sont négatives et qu'elles varient avec la longueur du groupe alcoyle de l'alcool.

Zusammenfassung — Die Verhältnisse der Mischungsenthalpie und des überschüssigen Molvolumens gegenüber der Zusammensetzung wurden bei 313.15 K an binären Systemen von 2,4,6-Kollidin mit normalen aliphatischen Alkoholen untersucht. Es wurde festgestellt, daß bei der gegebenen Temperatur H^E und V^E negativ sind und sich mit der Länge der Alkylgruppe des Alkohols ändern.

Резюме — Исследованы энтальпии смешения и избыточного мольного объёма смешения бинарных систем 2,4,6-коллидин — н-алифатические спирты в зависимости от их состава при температуре 313,15 К. Установлено, что H^E и V^E отрицательны и изменяются по величине в зависимости от длины алкильного радикала спирта.