Journal of Thermal Analysis and Calorimetry, Vol. 70 (2002) 251–254

EXCESS MOLAR ENTHALPIES AT 298.15 K OF THE BINARY MIXTURES *Tert*-butyl methyl ether+alcohol (*n*=1, 2, 3, 5)

S. M. Cebreiro[1], *M. Illobre*[1], *M. M. Mato*[1], *P. V. Verdes*[1], *J. L. Legido*[2] *and M. I. Paz Andrade*[1]

[1]Laboratory of Microcalorimetry, Department of Applied Physics, Faculty of Physics, University of Santiago, 15782 Santiago de Compostela, A Coruna, Spain
[2]Department of Applied Physics, Faculty of Sciences, University of Vigo, 36200 Vigo, Pontevedra, Spain

Abstract

We have determined the excess molar enthalpies H_m^E at 298.15 K and normal atmospheric pressure for the binary mixtures containing *tert*-butyl methyl ether (MTBE)+(methanol, ethanol, 1-propanol, 1-pentanol) using a Calvet microcalorimeter.

Keywords: alcohol, excess molar enthalpies, *tert*-butyl methyl ether

Introduction

We have determined the excess molar enthalpies of MTBE+(methanol, ethanol, 1-propanol, 1-pentanol) mixtures at the temperature of 298.15 K and atmospheric pressure. Values of excess molar enthalpies over the entire range of composition were measured using a Calvet microcalorimeter. The results were adjusted by variable-degree polynomials. Several H_m^E data have been published in the literature for MTBE + (methanol, ethanol, 1-propanol) [1–4] but as far as we know, there exist no previous measurements on mixtures MTBE + 1-pentanol in the literature.

Experimental

The sources and the purities of the chemicals substances employed were: MTBE (Aldrich >99.8%), methanol (Fluka >99.8%), ethanol (Scharlau >99.8%) 1-propanol (Aldrich > 99.8%), 1-pentanol (Aldrich >99%). Before measurements, all liquids were subjected to no further purification other than drying with Union Carbide 0.4 nm molecular sieves.

The experimental excess molar enthalpies were determined using a Calvet microcalorimeter with a calorimeter-cell volume of approximately 10 cm^3 and equipped with a device allowing operation in the absence of vapour phase linked to a

1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Philips PM2535 voltmeter and to a data acquisition system. The microcalorimeter was calibrated electrically using a stabilised current source (EJP-30, Setaram). The performance of the apparatus and procedures was checked by determining excess enthalpies for the standard system *n*-hexane + cyclohexane at 298.15 K and our results differ by less than 1 per cent from those of McGlashan and Stoeckli [5]. Both the calibration and operation conditions are described by Paz Andrade *et al.* [6–7]. The samples were prepared by mass using a Mettler H51 balance with a precision of $\pm 10^{-5}$ g covering the whole composition range of the mixtures. The precision of the excess molar enthalpies is estimated to better than 1 per cent. All molar quantities are based on the IUPAC relative atomic mass table [8].

Table 1 Excess molar enthalpies at 298.15 K

x	H^E_m/ J mol^{-1}	x	H^E_m/ J mol^{-1}	x	H^E_m/ J mol^{-1}	x	H^E_m/ J mol^{-1}	x	H^E_m/ J mol^{-1}
				x MTBE + (1–x) methanol					
0.0171	–6	0.0398	–3	0.2491	105	0.4967	296	0.8708	247
0.0173	–3	0.0654	3	0.3098	153	0.5277	309	0.9326	153
0.0367	–5	0.0958	15	0.4130	228	0.7290	353	0.9401	134
0.0390	–3	0.2387	99	0.4481	260				
				x MTBE + ethanol					
0.0323	34	0.1837	223	0.4660	461	0.7090	522	0.8680	376
0.0647	76	0.2237	272	0.5243	492	0.7699	493	0.8902	337
0.1002	115	0.2411	285	0.5910	527	0.8127	449	0.9628	138
0.1382	164	0.2676	317	0.6843	529	0.8130	461	0.9748	97
0.1752	216								
				x MTBE + 1-propanol					
0.0385	43	0.2072	302	0.3291	454	0.6008	564	0.7915	471
0.1012	138	0.2463	348	0.3796	497	0.6594	556	0.8583	395
0.1378	193	0.2919	410	0.4952	555	0.7904	472	0.9095	285
0.1716	243								
				x MTBE + 1-pentanol					
0.0580	39	0.1707	219	0.3051	417	0.6002	594	0.7964	499
0.0654	50	0.1942	266	0.3604	486	0.6515	596	0.8545	417
0.0950	102	0.2216	312	0.4399	541	0.7078	565	0.8957	328
0.1102	122	0.2638	363	0.5461	587	0.7643	523	0.9432	208
0.1562	200	0.2928	405						

Results and discussion

Experimental values of H_m^E for the four mixtures MTBE+(methanol, ethanol 1-propanol, 1-pentanol) are listed in Table 1. The experimental results for each mixture were fitted with a variable-degree polynomial, suggested by Redlich and Kister [9], of the form:

$$H_m^E = x(1-x)\sum_{i=1}^{n} A_i (2x-1)^{i-1} \quad (1)$$

where H_m^E/J mol^{-1}. The coefficients A_i was determined by an unweighted least-squares method using the Marquardt algorithm [10]. The degree of the polynomial used in Eq. (1) for each mixture has been determined applying an F test [11]. The parameters A_i and the standard deviations $s(H_m^E)$ are summarized in Table 2. A graphical representation of the experimental values of H_m^E plotted against x together with the smoothing curves are shown, in Fig. 1.

Table 2 Values of A_i and standard deviations for H_m^E

A_1	A_2	A_3	A_4	A_5	A_6	s
			MTBE + methanol			
1180	1232	71	174			3
			MTBE + ethanol			
1934	979	937	578	–353		4
			MTBE + 1-propanol			
2226	534	361	1073			4
			MTBE + 1-pentanol			
2294	831	442	576	–514	762	4

The experimental excess molar enthalpies, H_m^E are positive for all the studied systems over the whole range of composition, except for MTBE+methanol mixture where for low MTBE concentration the enthalpies are negative. This suggests the predominance of the rupture of the existing hydrogen bonds of the pure alcohol instead of the establishment of new interaction during the mixing process, given that the hydrogen bond established between an alcohol and the MTBE is weaker than that present in the pure alcohol.

The obtained curves are asymmetric, with their maximum around the rich compositions in MTBE. The maximum values of the excess molar enthalpies increase with the number of carbon atoms of the alcohol.

Several authors have measured H_m^E for *tert*-butyl methyl ether+alcohol (methanol, Tusel-Langer *et al.* [1]; ethanol, Nagata [2] and Zhu *et al.* [4], 1-propanol, Nagata *et al.* [3] and Zhu *et al.* [4]. The experimental values are in agreement with literature. As far as we know, there exist no previous measurements on mixtures MTBE+1-pentanol.

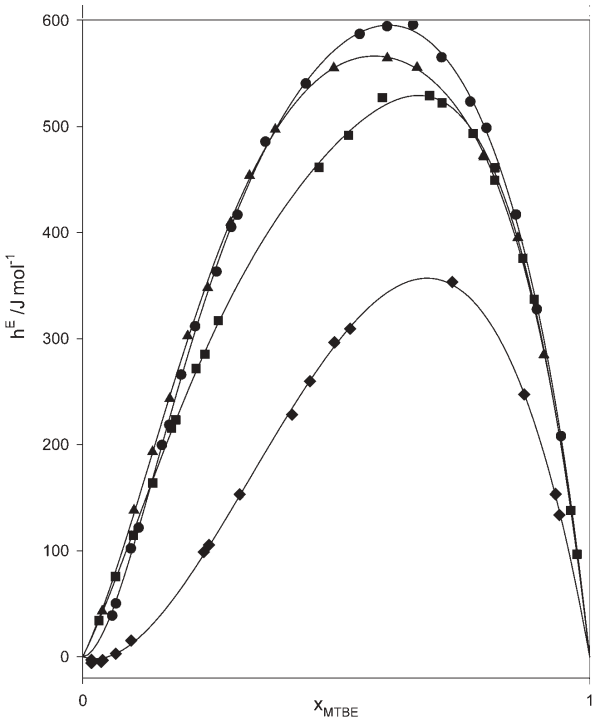

Fig. 1 Excess molar enthalpies H_m^E against mole fraction x at 298.15 K for: x MTBE + (1–x) alcohol. Experimental results: ◆ – methanol, ■ – ethanol, ▲ – 1- propanol, ● – 1-pentanol. — adjusted Redlich-Kister

References

1 E. Tusel-Langer, J. M. García Alonso, M. A. Villamañán Olfos and R. N. Lichtenthaler, J. Sol. Chem., 20 (1991) 153.
2 I. Nagata, J. Chem. Thermodyn., 26 (1994) 1137.
3 I. Nagata and K. Tamura, J. Chem. Thermodyn., 27 (1995) 1067.
4 S. Zhu, S. Shen, G. C. Benson and B. C.-Y. Lu. Fluid Phase Equilibria, 94 (1994) 217.
5 M. L. McGlashan and H. T. Stoeckli, J. Chem. Thermodyn., 1 (1969) 589.
6 M. I. Paz Andrade, S. Castromil and M. C. Baluja, J. Chem. Thermodyn., 2 (1970) 775.
7 M. I. Paz Andrade, Les Dévelopements Récents de la Microcalorimétrie et de la Thermogenèse, 1st Ed. CRNS, Paris, 1967.
8 IUPAC, Pure and Appl. Chem., 58 (1986) 1677.
9 O. Redlich, A. T. Kister, Ind. Eng. Chem., 40 (1948) 345.
10 D. W. Marquardt, An Algorithm for least Squares Estimation of Non- Linear Parameters. J. Soc. Ind. Appl. Math., 2 (1963) 431.
11 P. Bevington, Data Reduction and Error Analysis for the Physical Sciences. McGraw-Hill, New York 1969.