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Excess enthalpies of binary mixtures of methyl *tert.*-butyl ether (MTBE) with benzene, chlorobenzene, benzonitrile, and nitrobenzene at 298.15 K

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Abstract

Excess enthalpies have been measured for the binary mixtures MTBE + benzene, +chlorobenzene, +benzonitrile, and +nitrobenzene at 298.15 K using a Parr 1451 solution calorimeter. While the excess enthalpies of MTBE + benzene are positive, those for MTBE + chlorobenzene and MTBE + benzonitrile are negative. Those for MTBE + nitrobenzene change sign from positive to negative at higher mole fractions of MTBE. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Excess enthalpy; MTBE; Benzene; Substituted benzenes

1. Introduction

The present work forms a part of our study on the thermodynamic properties of binary liquid mixtures containing an ether and benzene or substituted benzenes. The experimental vapour–liquid equilibrium data for the binary systems anisole + benzene, +chlorobenzene, +benzonitrile, and +nitrobenzene have already been reported [1,2]. Excess enthalpies for the above binary systems have also been reported [3]. This paper presents measurements on the excess enthalpies of MTBE + benzene, +chlorobenzene, +benzonitrile, and +nitrobenzene, on which no published information is available.

2. Experimental

A Parr 1451 solution calorimeter was used for the measurement of excess enthalpies. Details of the calorimeter can be found in our earlier papers [4,5]. The reliability of the apparatus and of the method has been established by measuring the excess enthalpies for the systems benzene + carbon tetrachloride and toluene + chlorobenzene over the entire composition range at 298.15 K. Our results are in agreement with the literature data [6,7] within ±1%.

3. Materials

All the chemicals used in this work, except benzene, were procured from Fluka with a guaranteed purity of >99% (GC). HPLC grade benzene was supplied by Spectrochem (Mumbai, India). No further purification of the chemicals was attempted. The purity of the chemicals was ascertained by measuring some of the physical properties. From a comparison with the literature data [8–10] given in Table 1, the purity of the substances used in the present study is expected to be about 99.5%.

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Table 1
Comparison of physical properties of pure liquids with literature data

Substance	Density/303.15 K (g cm^{-3})	Refractive index/293.15 K	Reference
MTBE	0.7425	1.3690	This work
	0.7418	1.3690	[9,10]
Benzene	0.8684	1.5010	This work
	0.86829	1.50112	[8]
Chlorobenzene	1.0951	1.5250	This work
	1.0955	1.52481	[8]
Benzonitrile	0.9965	1.5290	This work
	0.99628	1.52823	[8]
Nitrobenzene	1.1937	1.5530	This work
	1.19341	1.5526	[8]

4. Results and discussion

The experimental results of excess enthalpies for the binary mixtures at 298.15 K are given in Table 2 and shown in Fig. 1. The results were fitted by the method of least squares to the equation

$$H^{\mathrm{E}}(\mathrm{J\,mol^{-1}}) = x(1-x)\sum h_j(2x-1)^j,$$

where x represents the mole fraction of MTBE. The values of the coefficients h_j and the standard deviation $\sigma(H^{\mathrm{E}})$ representing the fit of each set of results are given in Table 3. The standard deviation has been calculated using the relation $\sigma(H^{\mathrm{E}}) = \left[\sum\left(H^{\mathrm{E}}_{\mathrm{exp}} - H^{\mathrm{E}}_{\mathrm{cal}}\right)^2/(n-1)\right]^{1/2}$ where n represents the number of data points.

The excess enthalpies are positive for MTBE + benzene (maximum H^{E} of 148.4 J mol^{-1}), while for MTBE + chlorobenzene and MTBE + benzonitrile they are negative (maximum H^{E} of −412.7 and −253.0 J mol^{-1}, respectively). MTBE + nitrobenzene shows a change in sign of

Table 2
Excess molar enthalpies, H^{E}, of binary mixtures of MTBE at 298.15 K

x_1 MTBE (1)	H^{E} (J mol^{-1}) + benzene (2)	x_1 MTBE (1)	H^{E} (J mol^{-1}) + chlorobenzene (2)	x_1 MTBE (1)	H^{E} (J mol^{-1}) + benzonitrile (2)	x_1 MTBE (1)	H^{E} (J mol^{-1}) + nitrobenzene (2)
0.0632	60.1	0.0569	−92.4	0.0814	−63.9	0.0649	49.2
0.1330	104.3	0.1311	−190.2	0.1290	−105.4	0.1354	79.6
0.2022	130.2	0.1983	−264.8	0.1972	−155.8	0.1967	94.3
0.2727	147.0	0.2744	−328.9	0.2823	−197.8	0.2863	94.9
0.3654	153.9	0.3718	−381.6	0.3570	−220.6	0.3663	84.2
0.4312	151.0	0.4226	−402.0	0.4206	−240.2	0.4174	74.0
0.4977	142.6	0.4884	−412.7	0.4931	−253.0	0.4922	57.0
0.5025	148.4	0.5147	−384.3	0.5707	−216.5	0.5055	51.9
0.5755	141.3	0.5682	−391.1	0.6378	−214.1	0.6079	26.2
0.6547	127.7	0.6466	−385.3	0.7214	−196.0	0.6495	13.2
0.7354	105.5	0.7257	−354.0	0.7834	−170.4	0.7342	−11.5
0.7823	87.0	0.7961	−302.0	0.8543	−130.6	0.7899	−21.2
0.8620	57.7	0.8597	−230.4	0.9336	−68.1	0.8356	−28.4
0.9327	29.4	0.9140	−150.8			0.9183	−26.5

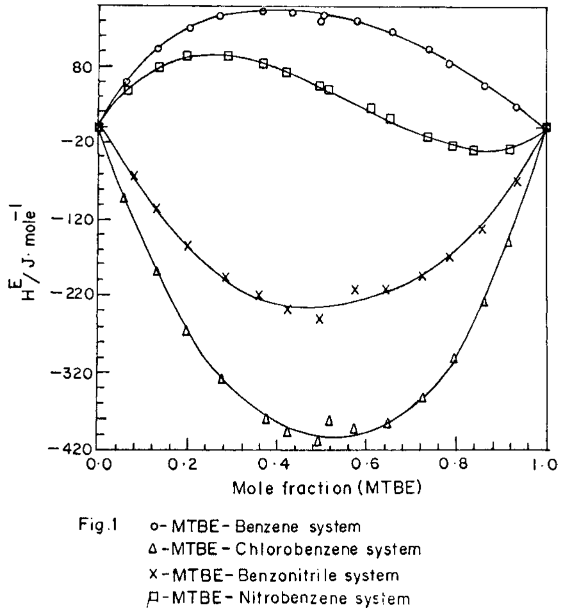

Fig. 1. (○) MTBE–benzene system; (△) MTBE–chlorobenzene system; (×) MTBE–benzonitrile system; (□) MTBE–nitrobenzene system.

excess enthalpies from positive to negative at higher mole fractions of MTBE (maximum negative H^E of -28.4 J mol^{-1}).

Certain similarities have been observed between the binary systems formed from anisole and MTBE. The excess enthalpies are positive both in the anisole + benzene and MTBE + benzene systems, though differing in magnitude. The change in sign of excess enthalpies for MTBE + nitrobenzene is also found in anisole + nitrobenzene system. Despite the similarities, certain differences have also been observed. While excess enthalpies for MTBE + chlorobenzene are more negative than MTBE + benzonitrile, the excess enthalpies for anisole + chlorobenzene are much less negative than those for anisole + benzonitrile.

The presence of electron pair donor–electron pair acceptor (EPD/EPA) type of interactions has been suggested in a variety of systems involving an ether and an aromatic compound [11,12]. Other type of interactions, namely dipole–dipole and dipole–induced dipole, are of much less significance owing to the fact that both the pairs: anisole–MTBE and benzonitrile–nitrobenzene have similar dipole moments but widely differing excess enthalpies in their binary systems.

Interactions of the O–Cl type have been shown to be very strong in binary systems involving ether and certain chloro-aromatic compounds [13] and their strength is estimated to be -1.1 kJ mol^{-1}. Such interactions are expected to be much stronger in MTBE + chlorobenzene system when compared to anisole + chlorobenzene system, in which the charge density on the donor ‘O’ atom of anisole is decreased due to electron delocalization into the ring. With MTBE, however the question of delocalization does not arise. Hence the presence of strong O–Cl interaction in MTBE + chlorobenzene is sufficient to reverse the trend found in anisole systems.

If EPD/EPA type of interactions are more important than any other type of interaction, then MTBE + nitrobenzene should show great magnitude of negative excess enthalpies than MTBE + benzonitrile, as nitro groups are better electron-acceptors than cyano groups [14]. Since this is not the case, it is postulated that the ‘size effect’ factor, written in the following expression [15]

$$H^E_{\text{observed}} = H^E_{\text{size effect}} + H^E_{\text{interaction}}$$

for nitrobenzene more than compensates for the ‘inter-

Table 3
Parameters h_j and standard deviation $\sigma(H^E)$ for different binary systems

System	Parameters					
	h_0	h_1	h_2	h_3	h_4	$100\sigma(H^E)$
MTBE + benzene	593.58	−180.47	192.27	−182.47	–	2.01
MTBE + chlorobenzene	−1608.55	−130.33	−551.05	−13.18	351.75	2.54
MTBE + benzonitrile	−946.66	99.71	−224.41	−339.53	260.96	3.49
MTBE + nitrobenzene	220.00	−534.91	−8.94	−202.60	–	4.82

action' factor, due to the large size of nitrobenzene molecule. Such size effect problems are not encountered in the other benzenes.

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