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Excess Enthalpies for Anisole + Benzene, + Chlorobenzene, + Benzonitrile, and + Nitrobenzene at 298.15 K

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Excess molar enthalpies for the binary systems anisole + benzene, + chlorobenzene, + benzonitrile, and + nitrobenzene have been measured at 298.15 K with a Parr 1451 solution calorimeter. While the excess enthalpies are positive for benzene, those for chlorobenzene and benzonitrile are negative. The excess enthalpies for anisole + nitrobenzene change sign.

Introduction

The present investigation is in continuation of our studies (Viswanathan et al., 1995a,b) on the thermodynamic properties of binary mixtures containing anisole and substituted benzenes. Excess volumes and isentropic compressibilities for anisole + benzonitrile and anisole + nitrobenzene have been reported (Rajkumar et al., 1985); the excess viscosities and excess volumes for anisole + chlorobenzene and anisole + nitrobenzene have also been reported (Joshi et al., 1990) in the literature. However, no excess molar enthalpy measurements have been reported on the above systems. This paper presents results for excess molar enthalpies for anisole + benzene, + chlorobenzene, + benzonitrile, and + nitrobenzene at 298.15 K.

Experimental Section

All the chemicals used in this study, except benzene, were obtained from Fluka with a guaranteed purity of >99% (GC). Benzene (spectroscopic grade) was obtained from SD Fine Chemicals (India). No further purification of the chemicals was attempted. The purity of the chemicals was ascertained by measuring some of the physical properties. A comparison with the literature values (Riddick et al., 1986; Dilke et al., 1950) is given in Table 1.

The excess enthalpies were measured using a Parr 1451 solution calorimeter. Details of the calorimeter and the experimental procedure were described earlier (Vijayakumar et al., 1995a,b). The reliability of the apparatus and of the method was established by measuring the excess enthalpies for benzene + carbon tetrachloride and toluene + chlorobenzene over the entire composition range at 298.15 K. Our results are in agreement with the literature data (Stokes et al., 1969; Tanaka and Benson, 1976) within 1%.

Results and Discussion

The experimental results of excess molar enthalpies $H^{\mathrm{E}}_{\mathrm{m}}$ for anisole + benzene, + chlorobenzene, + benzonitrile, and + nitrobenzene at 298.15 K are given in Table 2 and shown in Figure 1. The results were fitted by the

Table 1. Comparison of Experimental Densities, ρ, and Refractive Indices, n_{D}, with the Literature Values

	ρ(kg·m^{-3}) at 303.15 K		n_{D} at 293.15 K	
component	present work	lit.[a]	present work	lit.[a]
anisole	994.0[c]	994.02[c]	1.5175	1.517 00
benzene	868.4	868.29	1.5010	1.501 12
chlorobenzene	1095.1	1095.50	1.5250	1.524 81
benzonitrile	996.5	996.28	1.5290	1.528 23
nitrobenzene	1193.7	1193.41	1.5530	1.552 6[b]

[a] Riddick et al. (1986). [b] Values from Dilke et al. (1950). [c] Values at 293.15 K.

Table 2. Excess Molar Enthalpies $H^{\mathrm{E}}_{\mathrm{m}}$ of Binary Mixtures at 298.15 K

x	$H^{\mathrm{E}}_{\mathrm{m}}$/(J·mol^{-1})	x	$H^{\mathrm{E}}_{\mathrm{m}}$/(J·mol^{-1})
x anisole + (1 − x) benzene		x anisole + (1 − x) chlorobenzene	
0.0605	18.9	0.0744	−3.8
0.1259	36.3	0.1290	−5.3
0.2033	46.8	0.1961	−7.2
0.2805	55.7	0.2790	−8.6
0.3791	60.2	0.3591	−9.1
0.4266	61.9	0.4283	−9.1
0.5058	80.2	0.4941	−7.3
0.5832	79.5	0.5797	−6.2
0.6553	73.5	0.6621	−5.0
0.7473	64.2	0.7589	−3.4
0.8150	49.0	0.8508	−1.9
0.8773	32.8	0.9317	−0.6
0.9330	17.7		
x anisole + (1 − x) benzonitrile		x anisole + (1 − x) nitrobenzene	
0.0528	−19.7	0.0782	−3.1
0.1380	−43.4	0.1475	−7.4
0.2009	−58.5	0.2061	−11.0
0.2779	−69.7	0.2768	−15.0
0.3670	−78.0	0.3702	−18.7
0.4342	−79.5	0.4336	−20.1
0.5006	−85.4	0.4980	−20.1
0.5776	−85.2	0.4986	−20.1
0.6487	−81.1	0.5653	−18.6
0.7340	−70.6	0.6480	−14.5
0.8037	−57.7	0.7339	−8.6
0.8804	−38.9	0.7985	−3.7
0.9463	−17.4	0.8583	−0.2
		0.9216	3.1
		0.9500	4.4

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Table 3. Parameters h_j and Standard Deviation $\sigma(H_m^E)$ from Eq 1 (T = 298.15 K)

	parameters						
system	h_0	h_1	h_2	h_3	h_4	h_5	$100\sigma(H_m^E)$
x anisole + (1 − x) benzene	293.57	182.15	75.56	−570.94	−71.51	387.09	4.70
x anisole + (1 − x) chlorobenzene	−30.91	25.13	−1.26				6.11
x anisole + (1 − x) benzonitrile	−342.53	−37.43	−40.88	79.36			2.42
x anisole + (1 − x) nitrobenzene	−79.62	24.40	74.10	22.26	72.03	45.16	2.99

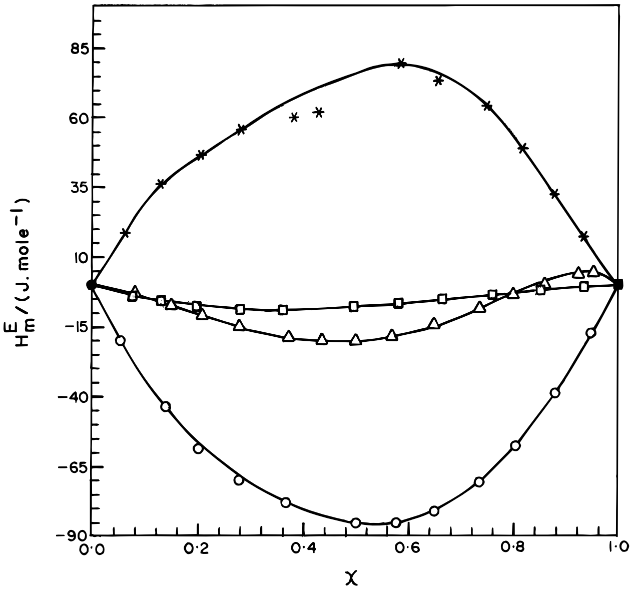

Figure 1. H_m^E versus the mole fraction of anisole (x) at 298.15 K: (*) anisole (x) + benzene (1 − x), (□) anisole (x) + chlorobenzene (1 − x), (○) anisole (x) + benzonitrile (1 − x), (△) anisole (x) + nitrobenzene (1 − x).

method of least squares to the equation

$$H_m^E/(\mathrm{J{\cdot}mol^{-1}}) = x(1-x)\sum h_j(2x-1)^j \qquad (1)$$

where x is the mole fraction of anisole. The values of the coefficients h_j and the standard deviation $\sigma(H_m^E)$ representing the fit of each set of results are given in Table 3. The standard deviation has been calculated using the relation

$$\sigma(H_m^E) = [[\sum\{(H_m^E(\mathrm{exp}) - H_m^E(\mathrm{calcd}))/H_m^E(\mathrm{exp})\}^2]/(n-p)]^{1/2} \qquad (2)$$

where n and p represent the number of results and number of parameters, respectively.

The excess enthalpies are positive for anisole + benzene (maximum H_m^E of 80.2 J·mol^{-1}), while for anisole + benzonitrile they are negative (maximum negative H_m^E of −85.4 J·mol^{-1}). Anisole + chlorobenzene shows very small negative excess enthalpies (maximum negative H_m^E of −9.1 J·mol^{-1}). Anisole + nitrobenzene shows a change in sign of excess enthalpies from negative to positive at higher mole fractions of anisole (maximum negative H_m^E of −20.1 J·mol^{-1}).

Our results of H_m^E for anisole + benzonitrile and anisole + nitrobenzene depart from the pattern expected from earlier works. The results of excess volumes and excess isentropic compressibilities for the aforementioned systems have been discussed (Rajkumar et al., 1985; Srivastava, 1992) in terms of a possible donor−acceptor (D−A) interaction involving anisole as the donor. Further, the magnitudes of both the excess properties are higher for the latter system, in agreement with the view (Briegleb, 1964) that nitro groups are better acceptors than cyano groups. Our results for the above systems are just the opposite: whereas anisole + benzonitrile shows appreciable negative H_m^E values, anisole + nitrobenzene shows a sign change in H_m^E from negative to positive, and the negative values too are of small magnitude. It, therefore, seems reasonable to assume that some other factors are additionally responsible for this observation.

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