

Excess enthalpies of dimethylsulfoxide with substituted benzenes at 298.15 K

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Abstract

Excess molar enthalpies (H^E) at 298.15 K have been measured by a Paar 1451 solution calorimeter as a function of composition for the binary liquid mixtures of dimethylsulfoxide (DMSO) with substituted benzenes. The substituted benzenes include toluene, ethylbenzene, chlorobenzene, bromobenzene and nitrobenzene. The H^E values for the above mixtures are all positive over the entire composition range. The experimental results have been correlated using the Redlich–Kister (R–K) polynomials. The results are interpreted on the basis of possible hydrogen bonding between unlike molecules and changes in molecular association equilibria as well as structural effects for these systems. The excess enthalpy data have also been correlated with the Peng–Robinson (PR) as well as the Patel–Teja (PT) equations of state (EOS) and also the activity coefficient models of the Wilson and the NRTL.

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1. Introduction

Experimental data of excess thermodynamic properties of liquids and liquid mixtures are of great fundamental and practical importance. These properties allow one to draw information on the structure and interactions of mixed solvents. The chemical industries have recognized the importance of the thermodynamic properties in design calculations involving chemical separations, heat transfer, mass transfer and fluid flow. Dimethylsulfoxide (DMSO) is a highly polar ($\mu = 4.06$ Debye) [1] and self-associated solvent [2] and has ability to participate in hydrogen bonding [3]. It has a large dipole moment, high dielectric constant ($\epsilon = 46.45$) [1] and polarizability [4] and these enable to stabilize molecules and ions through dipole and induced-dipole interactions. In liquid mixtures, the enhancement of its donor

ability may result from the breaking of DMSO structure by the addition of second liquid component [5]. It is less toxic and an effective paint stripper, being much safer than many of the other polar solvents. Since, DMSO as a solvent of its high boiling point, thus its solutions are not typically evaporated but instead diluted to isolate the reaction product.

In recent years the thermodynamic properties of dimethylsulfoxide (DMSO) with substituted benzenes have received increasing attention because they serve as model compounds in biochemical considerations [6–8]. The excess molar enthalpy (H^E) of binary mixtures containing DMSO + cycloethers [9], +hexamethylphosphoric trimide [10], +water [11], +dialkylethers [12], +halogenized aromatic compounds [13,14], +dihalogenized benzenes [15], +*N,N*-dimethylethanolamine [16], +alkylbenzenes [17], +1-alkynes [18], +alkane-1-amines [19], +aliphatic alcohols [20], +aliphatic alcohols or aliphatic nitriles [21], +normal alcohols [22], +ketones [23] have been appeared in the literature. However, no effort appears to have been made to collect the H^E for the mixtures of DMSO with substituted benzenes and there is no evidence for specific interactions of DMSO with substituted benzenes. In addition, these

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liquids were chosen in the present investigation on the basis of their industrial importance. DMSO, toluene, ethylbenzene, chlorobenzene, bromobenzene and nitrobenzene are important liquids which find a variety of applications such as solvents for lacquers, oils and resins [4,6].

In order to extend our research programs to explore the interactions between the highly polar groups with other solvents [6,23–30], and to characterize the type and the magnitude of molecular interactions between the polar group solvents, we report here the H^E at $T = 298.15$ K and atmospheric pressure of binary mixtures containing DMSO with toluene, ethylbenzene, chlorobenzene, bromobenzene and nitrobenzene. Moreover, the experimental H^E data were correlated with the Peng–Robinson (PR) [31] and the Patel–Teja (PT) [32] equations of state and also the activity coefficient models of the Wilson [33] and the NRTL [34] for the binary systems.

2. Experimental

2.1. Materials

The pure solvents of highest purity commercially available were used in the present investigation. DMSO and substituted benzenes were purified by the standard methods described by Riddick et al. [1]. The purity of the samples was checked by measuring densities and boiling points. The densities were measured using a standard bicapillary pycnometer, giving an accuracy of 2 parts in 10^5 . Boiling points at 95.3 kPa were measured by Swietoslawski-type ebulliometer [35] with an accuracy of ± 0.2 K. The measured values are in good agreement with literature values [1,36] and are included in Table 1.

2.2. Method

The H^E values of liquid mixtures were measured using a Paar 1451 solution calorimeter. The measurements were performed in an isolated house at 298.15 K and atmospheric pressure. The detailed procedure and apparatus used in this work have been depicted in our previous papers [25,37]. In the measurement of excess enthalpies, known mass of 100 cm^3 of one component A as solvent was taken into the Dewar vessel and 20 cm^3 of other component B as solute was weighted in a sealed glass

Table 1
Properties of pure components: boiling points temperatures (T) at atmospheric pressure and densities (ρ) at 303.15 K

Component	T (K)		ρ (g cm^{-3})	
	This work	Literature ^a	This work	Literature
DMSO	462.19	462.15	1.09240	1.09142 ^b
Toluene	383.05	383.78	0.85766	0.85770 ^a
Ethylbenzene	408.75	409.34	0.85820	0.85820 ^a
Chlorobenzene	404.35	404.85	1.09552	1.09550 ^a
Bromobenzene	427.85	429.19	1.48148	1.48150 ^a
Nitrobenzene	483.05	483.95	1.19340	1.19341 ^a

^a Ref. [1].

^b Ref. [36].

rotating cell. Both the components were kept in thermal contact with each other in the Dewar mixing chamber at 298.15 K. After attaining the thermal equilibrium component B in the rotating cell was mixed with component A in the Dewar vessel by pushing the glass rod. The temperature change accompanying the mixing process was sensed by the thermistor and recorded on the strip chart recorder. These experiments were continued until the concentrations reach 50 to 60% and then this procedure was repeated by taking solvent as solute and solute as solvent. The reliability of the apparatus and the method was established by measuring H^E values of standard systems, i.e., benzene with carbontetrachloride and chlorobenzene with toluene throughout the concentration range at 298.15 K. Results were in good agreement with the reported data in the literature [38]. The uncertainty of the measured H^E values is $\pm 1\%$.

3. Results

The measured H^E values of DMSO with substituted benzenes at 298.15 K are reported in Table 2 and shown graphically in Fig. 1 as a function of mole fraction of substituted benzenes. The experimental H^E results of each binary system were fitted with the smoothing functions by the Redlich–Kister (R–K) type equation using the polynomial form:

$$\frac{H^E}{\text{J mol}^{-1}} = x_1(1 - x_1) \sum_i h_i (2x_1 - 1)^i \quad (1)$$

where h_i are coefficients for the binary systems and are collected in Table 3 along with the percentage standard deviation. The values of the percentage standard deviation are computed from the relation:

$$\% \sigma(H^E) = \left[\frac{\sum_{i=1}^n [100 \times (H_{\text{calc},i}^E - H_{\text{expt},i}^E) / H_{\text{expt},i}^E]^2}{n - p} \right]^{0.5} \quad (2)$$

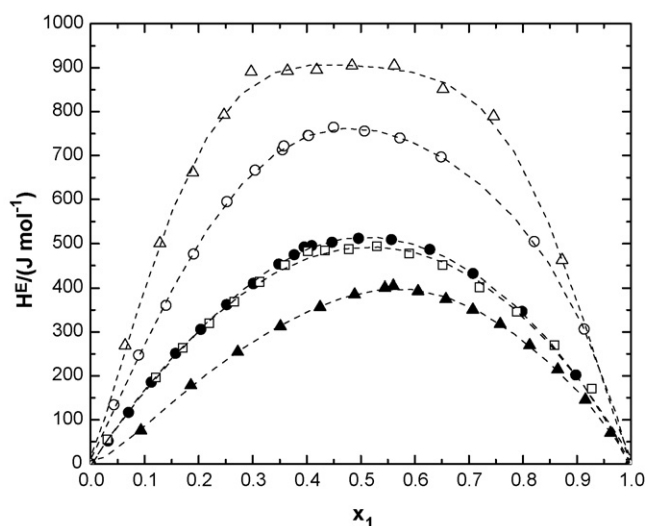


Fig. 1. Plot of excess molar enthalpies (H^E) against mole fraction of substituted benzenes (x_1) for DMSO + toluene (\circ), +ethylbenzene (Δ), +chlorobenzene (\square), +bromobenzene (\bullet), and + nitrobenzene (\blacktriangle) at 298.15 K and atmospheric pressure. Dashed lines (---) correlated by the Redlich–Kister equation.

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