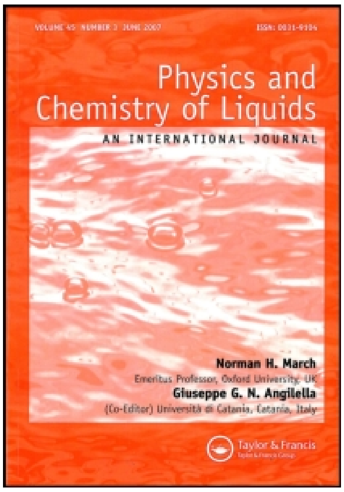

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Volumetric behaviour of binary liquid mixtures of dimethylsulphoxide with substituted benzenes at 303.15 k

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VOLUMETRIC BEHAVIOUR OF BINARY LIQUID MIXTURES OF DIMETHYLSULPHOXIDE WITH SUBSTITUTED BENZENES AT 303.15 K

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Excess molar volumes (V^E) for binary mixtures of dimethyl sulphoxide (DMSO) with substituted benzenes have been measured at 303.15 K. The substituted benzenes include toluene, ethylbenzene, chlorobenzene, bromobenzene and nitrobenzene. The measured V^E data is positive for the mixtures of DMSO with nitrobenzene and is completely negative over the entire composition range in the mixtures of toluene, ethylbenzene and chlorobenzene and an inversion in sign is observed in the bromobenzene system. The experimental results are analysed in terms of intermolecular interactions and effect of substitutents on benzene ring between unlike molecules.

Keywords: Binary mixtures; Excess volumes; Dimethylsulphoxides; Substituted benzene; Molecular interactions

1. INTRODUCTION

Knowledge of the thermodynamic properties of organic liquid mixtures is very important in understanding the molecular interactions between the components for theoretical models and also industrial applications. Further, thermodynamic properties of binary mixtures containing components which are capable of undergoing specific interactions, exhibit significant deviations from ideality arising not only from difference in molecular size and shape but also from structural changes. A literature survey has shown that V^E data for the binary mixtures of dimethylsulphoxide with 1-alkanols [1–3] and aromatic esters [4] have been reported earlier. Similarly, molecular interactions of DMSO with benzene toluene, chlorobenzene and bromobenzene were also reported earlier [5,6].

The present study is in continuation of our earlier research [7–9] on thermodynamic properties of binary liquid mixtures. The liquids were chosen in the present

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investigation on the basis of their industrial importance. Dimethyl sulphoxide, toluene, ethylbenzene, chlorobenzene, bromobenzene and nitrobenzene are important liquids which find a variety of applications such as solvents for lacquers, oils and resins. Also, the properties of DMSO have been the subject of considerable interest because of its versatility as a solvent and a plasticizer [1]. It is a highly polar aprotic [10] liquid which has the ability to participate in hydrogen bonding. The choice of DMSO as a common component in the present investigation was made because of its wide range of applicability as a solvent in chemical and biological processes involving both plants and animals. It is a highly polar aprotic solvent because of its S′–O group and has a large dipole moment and relative permittivity [11] ($\mu = 3.9\,\mathrm{D}$ and $\varepsilon = 46.6$ at 298.15 K). The present investigation was undertaken to study the effect of introduction of methyl, ethyl, chloro, bromo and nitro groups on benzene ring which in turn modifies the nature and degree of interaction between component molecules.

2. EXPERIMENTAL

All the chemicals used were of analytical grade. Dimethyl sulphoxide, toluene, ethylbenzene, chlorobenzene, bromobenzene and nitrobenzene were purified as reported earlier [12–14]. The purity of the sample 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 were measured using a swieltoslawski type ebulliometer [15] giving an accuracy of $\pm 0.2°\mathrm{C}$. The measured values are in good agreement with literature values [12,16] and are included in Table I. Excess volumes V^E were measured using the dilatometer of the type described earlier [17] and the measured V^E values were accurate to $\pm 0.003\,\mathrm{cm^3\,mol^{-1}}$.

3. RESULTS AND DISCUSSION

The experimental excess volumes (V^E) of five binary mixtures are given in Table II and shown in Fig. 1. V^E values were fitted to an empirical relation proposed by Redlich–Kister [18].

$$V^E \mathrm{cm^3/mol} = X_1(1 - X_1)[a_0 + a_1(2X_1 - 1) + a_2(2X_1 - 1)^2] \tag{1}$$

TABLE I Densities and boiling points of pure components at 303.15 K

Component	*Boiling point °K*		*Density (gm/cc)*	
	Experiment	*Literature*	*Experiment*	*Literature*
Dimethyl sulphoxide	460.95	462.15	1.09240	1.09135
Toluene	381.65	383.7	0.85766	0.85770
Ethylbenzene	406.95	409.34	0.85820	0.85820
Chlorobenzene	402.35	404.85	1.09552	1.09550
Bromobenzene	426.85	429.19	1.48148	1.48150
Nitrobenzene	483.05	483.95	1.19340	1.19341

TABLE II Mole fraction of dimethylsulphoxide (DMSO) and Excess Molar Volumes (V^E) for the binary mixtures of dimethylsulphoxide (1) with substituted benzenes (2) at 303.15 K

Mole fraction of DMSO (X_1)	V^E	V^E	V^E
	Experimental	*Redlich–Kister*	*Hwang*
		$cm^3\ mol^{-1}$	
DMSO + toluene			
0.1027	−0.085	−0.084	−0.083
0.2290	−0.182	−0.183	−0.184
0.3260	−0.242	−0.244	−0.245
0.4364	−0.286	−0.289	−0.289
0.5016	−0.306	−0.301	−0.301
0.6127	−0.292	−0.293	−0.292
0.7265	−0.246	−0.247	−0.246
0.8578	−0.152	−0.150	−0.151
0.9216	−0.086	−0.087	−0.088
DMSO + ethyl benzene			
0.1347	−0.076	−0.073	−0.074
0.2216	−0.126	−0.124	−0.125
0.3278	−0.174	−0.177	−0.179
0.4255	−0.210	−0.214	−0.215
0.5044	−0.232	−0.232	−0.232
0.6128	−0.237	−0.236	−0.235
0.7216	−0.216	−0.212	−0.210
0.8598	−0.138	−0.135	−0.136
0.9321	−0.071	−0.073	−0.074
DMSO + chlorobenzene			
0.1243	−0.009	−0.008	−0.008
0.2424	−0.019	−0.022	−0.022
0.3016	−0.030	−0.029	−0.029
0.4674	−0.043	−0.045	−0.045
0.5351	−0.052	−0.045	−0.047
0.6333	−0.048	−0.046	−0.045
0.7021	−0.041	−0.042	−0.041
0.8121	−0.027	−0.029	−0.029
0.9529	−0.008	−0.008	−0.008
DMSO + bromobenzene			
0.1268	−0.015	−0.016	−0.017
0.2431	−0.019	−0.017	−0.016
0.3264	−0.012	−0.013	−0.012
0.4272	−0.009	−0.004	−0.003
0.5463	0.012	0.009	0.008
0.6021	0.016	0.014	0.013
0.7063	0.024	0.021	0.020
0.8202	0.020	0.022	0.022
0.9315	0.013	0.013	0.014
DMSO + nitrobenzene			
0.1256	0.078	0.078	0.077
0.2597	0.139	0.140	0.140
0.3713	0.175	0.176	0.176
0.4399	0.192	0.190	0.189
0.5023	0.202	0.197	0.203
0.6113	0.191	0.195	0.200
0.7359	0.164	0.168	0.172
0.8214	0.132	0.131	0.136
0.9046	0.081	0.080	0.083

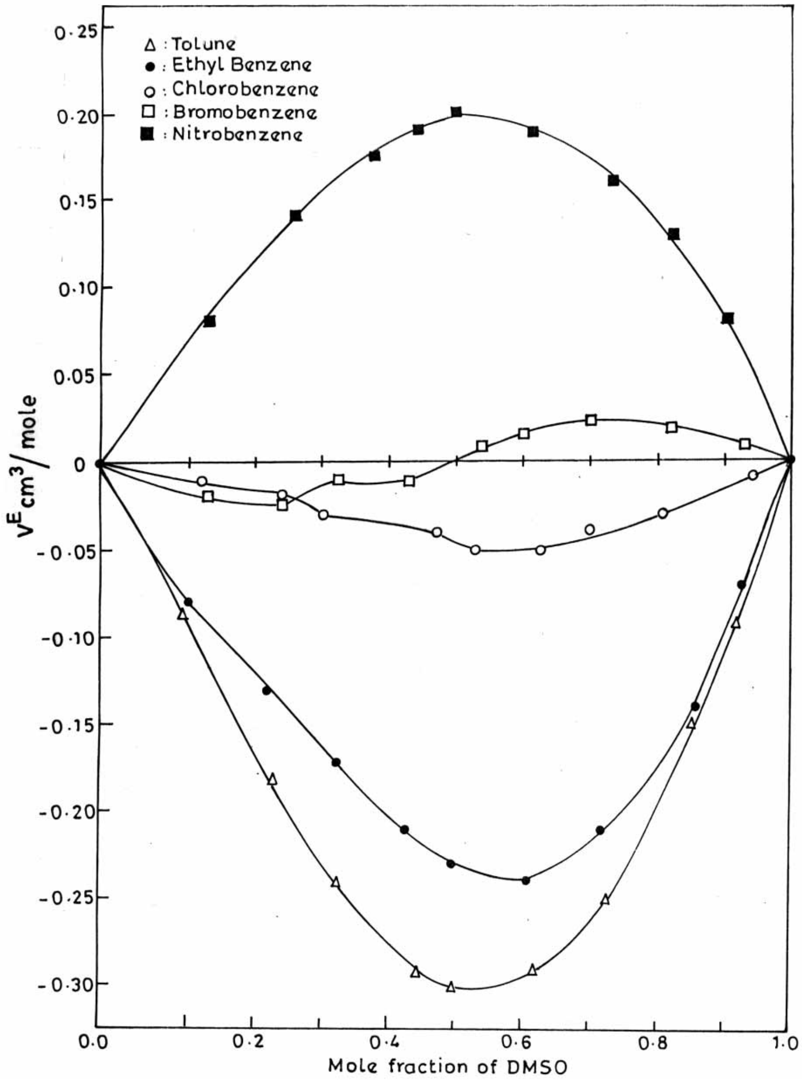

FIGURE 1 Excess volumes of dimethyl sulphoxide with substituted benzenes.

where a_0, a_1 and a_2 are adjustable parameters and X_1 is the mole-fraction of DMSO. The values of the parameters were estimated by the least-square method. Further, V^E results were also fitted to the semi-empirical equation proposed by Hwang *et al.* [19].

$$V^E \mathrm{cm}^3/\mathrm{mol} = X_1X_2[b_0 + b_1X_1^3 + b_1X_2^3] \qquad (2)$$

where X_1 and X_2 represent the mole fractions of DMSO and substituted benzenes and b_0, b_1 and b_2 are constants. The computation of "b" coefficients in the above equation was described earlier [20,21]. The values of the two sets of constants are given in Table III along with standard deviations, $\sigma(V^E)$. The standard deviation $\sigma(V^E)$,

TABLE III Standard deviation and values of constants from the Redlich–Kister Eq. (1) and Hwang *et al.* Eq. (2)

System	*Eq.(1)*				*Eq.(2)*			
	$cm^3\,mol^{-1}$				*$cm^3\,mol^{-1}$*			
	a_0	a_1	a_2	$\sigma(V^E)$	b_0	b_1	b_2	$\sigma(V^E)$
DMSO + toluene	– 1.2021	– 0.1884	0.2176	0.003	– 1.203	– 0.1969	0.2165	0.001
DMSO + ethylbenzene	– 0.9269	– 0.3266	0.0798	0.003	– 0.9246	– 0.322	0.0672	0.001
DMSO + chlorobenzene	– 0.1856	– 0.0743	0.0992	0.003	– 0.1823	– 0.0749	0.0911	0.005
DMSO + bromobenzene	0.0156	0.2137	0.0005	0.003	0.0130	0.2174	0.0116	0.001
DMSO + nitrobenzene	0.7852	0.1387	0.0515	0.003	0.7984	0.1676	0.0456	0.001

values given in Table III point out that the equation of Hwang *et al.* also represents precisely the V^E data. Furthermore, the predicted V^E values are also included in Table II along with experimental results.

Dimethyl sulphoxide is a highly polar compound because of its large dipole moment and polarizability [22] and this enables the stabilization of molecules and ions through dipole and induced-dipole interactions. Its high electron density on the unscreened oxygen atom enables it to solvate protons and other cations strongly. In liquid mixtures, the enhancement of its donor ability may result from the breaking of DMSO structure by the second liquid component [1].

The experimental V^E data in Table II can be explained as follows: According to Wisniak *et al.* [23] the sign and intensity of the volume changes that take place during mixing is the result of several effects that operate in the same or opposite directions. The most important ones are: (a) a positive one due to the break up of the structure of one or both components arising from non-chemical or chemical interactions such as hydrogen bonding or complex forming interactions such as self-association and (b) a negative one due to physical interaction like hetero-association or geometric fitting of one component into the second, leading to a more compact packing i.e., interstitial accommodation. The measured V^E data reveals that chemical interactions which contribute to the positive excess volume is dominant in the DMSO nitrobenzene mixture, whereas in the case of DMSO with toluene, ethylbenzene, chlorobenzene the negative V^E data indicates that structural effects are dominant over the entire composition range and both the effects are competing with each other to varying degrees in the mixture of DMSO with bromobenzene.

It is established that the sign and magnitude of V^E give a good estimate of the strength of the unlike interactions in a binary mixture [24]. Moreover, at the simplest qualitative level, the present V^E data can be explained if it is assumed that the electron donating power of benzene molecule will increase with the introduction of a methyl group (or) ethyl group in the ring. Likewise, electron donor–acceptor interactions takes place between DMSO and aromatic hydrocarbons. Experimental V^E data for the system DMSO with toluene is more negative than that of DMSO with ethylbenzene. This suggest that toluene moiety interacts strongly with DMSO than with ethylbenzene. Our experimental results support this conjucture. Furthermore, the molecular interactions operative between the two components are due to the residual electric moments and dispersion forces and may not significantly differ from those forces present in pure liquids. Hence, the non-ideality being reflected in the system studied is mainly due to geometrical factors, i.e. difference in molecular shape and size of the mixture components [25]. The negative V^E observed in the above two systems suggest that on mixing of these components, there is disturbance in the packing arrangements of pure liquids leading to contraction in volume.

The V^E data for the mixture of DMSO with chlorobenzene is negative over entire composition range and for bromobenzene, it exhibits an inversion in sign. This may be due to the smaller size of chlorine atom than bromine atom, though the dipole moments of the two halogen compounds are the same. This observation is similar to that of Prabhavathi *et al.* which was reported earlier [26]. The positive V^E values for DMSO nitrobenzene mixture when compared to those of halobenzenes may be due to the following reasons: [1] nitrogroup deactivates the benzene ring while chloro and bromo groups activate the benzene ring and [2] the viscous nature of nitrobenzene may cause more positive V^E values than chlorobenzene and bromobenzene. In addition to this, it is characterized by interactions between π-electron cloud of DMSO with the delocalized π-electron cloud over the nitrogen and oxygen atoms of the nitrogroup of nitrobenzene resulting in the formation of a weak p-complex.

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