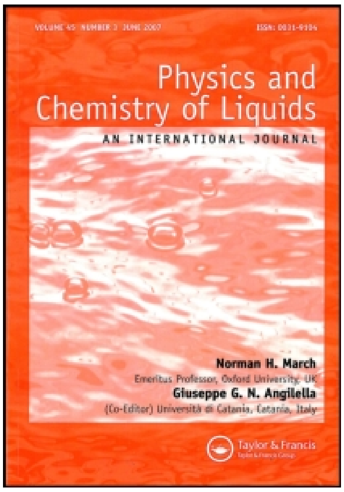

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Molecular Interaction Study on Binary Mixtures of Dimethyl Sulphoxide Isobutyl Methyl Ketone (IBMK), Acetylacetone and Tri-N-Butylphosphate (TBP) from the Excess Properties of Ultrasonic Velocity, Viscosity and Density

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MOLECULAR INTERACTION STUDY ON BINARY MIXTURES OF DIMETHYL SULPHOXIDE + ISOBUTYL METHYL KETONE (IBMK), + ACETYLACETONE AND + TRI-N-BUTYLPHOSPHATE (TBP) FROM THE EXCESS PROPERTIES OF ULTRASONIC VELOCITY, VISCOSITY AND DENSITY

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Excess isentropic compressibility (β_s^E), excess ultrasonic velocity (C^E), excess acoustic impedance (Z^E), excess intermolecular free-length (L_f^E) and excess viscosity (η^E) have been computed from the measured ultrasonic velocity, viscosity and density of the binary liquid mixtures of dimethyl sulphoxide (DMSO) with isobutyl methyl ketone (IBMK), acetylacetone and tri-n-butylphosphate (TBP) at 303.15 K. The results are discussed in terms of molecular interactions between the component liquids in different systems. The nature of variation of these excess parameters provides information about the type of interaction taking place in these binary systems.

KEY WORDS: DMSO solutions, ultrasonic velocity, viscosity, isentropic compressibility, acoustic impedance.

INTRODUCTION

Long chain aliphatic sulphoxides R_2SO in various diluents have been chosen as extractants[1-5] for many metal ions viz., uranium(VI), thorium(IV), actinides, lanthanides and various other metals. The simplest aliphatic sulphoxide namely dimethyl sulphoxide (DMSO) has been chosen in the present report to understand the molecular interaction between DMSO and some commercial extractants/diluents so that it can throw light on the nature of molecular interaction of long chain[2] aliphatic sulphoxide with extractants/diluents. In this laboratory studies have been made on the molecular interaction of tri-n-butyl phosphate (TBP)[6], which is a versatile extractant for PUREX process in processing of nuclear fuel, benzene, carbon tetrachloride, isobutyl methyl ketone, acetyl acetone and with long chain[2] aliphatic alcohols[7] used as modifiers in extractant studies using viscosity, density and ultrasonic measurements as probe. Ultrasonic studies of other commercial extractants with various diluents have also been made in order to understand molecular interaction. The acoustic properties of several binary mixtures have been computed with the related physico-chemical properties[9-11] and from this the assessment of the binary mixtures have been made. Ultrasonic velocity is an important parameter being frequently used to investigate the intermolecular interactions in the binary liquid mixtures[12-16]. The nature of variation of the derived thermodynamic properties such as isentropic compressibility, acoustic impedance, intermolecular free-length and viscosity and their excess properties provides a lot of valuable information about the molecular environments and the nature of interactions. Excess thermodynamic properties of the liquid mixtures depend on molecular association, dissociation and complex formation. This paper reports excess isentropic compressibility (β_s^E), excess intermolecular free length (L_f^E), excess acoustic impedance (Z^E), excess ultrasonic velocity (C^E) and excess viscosity (η^E) from ultrasonic velocity, viscosity and density measurements of binary mixtures of isobutyl methyl ketone (IBMK), acetyl acetone (HAA) and tri-n-butyl phosphate (TBP) with dimethyl sulphoxide (DMSO) at 303.15 K in order to understand molecular interactions.

MATERIALS AND METHODS

Dimethyl sulphoxide, tri-n-butyl phosphate, acetylacetone and isobutyl methyl ketone used were of analytical grade (E. Mecrk and BDH) and were purified by standard procedure described by Weissberger[17]. DMSO used was 99.5% pure and was further purified by using molecular seive and distillation. The purity of the samples was checked by comparing the measured densities with those reported in the literature[18-20].

Viscosity and density measurements were made by a calibrated Ostwald Viscometer and a bicapillary Pyknometer respectively. The densities of all the components were measured by a bicapillary Pyknometer calibrated at 303.15 K with deionised doube distilled water with 0.996 g cm^{-3} as its density at 303.15 K with a precision of 3 parts per 10^5. The ultrasonic velocity was measured by a single crystal variable path ultrasonic interferometer operating at 5 MHz frequency at 303.15 K circulating water from thermostatically regulated bath around the sample holder with double wall to maintain the temperature of the liquid constant with a precision of ±0.01 K. The accuracy of the interferometer is ±0.5 ms^{-1}. The viscometer was immersed in a constant temperature water bath maintained within ±0.02 K and the time of flow was determined, the height of the liquid column being observed with the help of a cathetometer. The values of viscosities so obtained were precise up to ±0.002 ($\times 10^{-3}$ Ns m^{-2}).

Table 1 Densities of pure components.

Compound	*Density, g cm^{-3} (303.15 K)*	
	Experimental	Literature
Dimethyl sulphoxide	1.0949	1.0958
Acetyl acetone	0.9661	0.973 (293 K)
Isobutyl methyl ketone	0.7913	0.7978 (293 K)
Tri-n-butyl phosphate	0.9700	0.9727 (298 K)

Binary mixtures of DMSO with isobutyl methyl ketone, acetyl acetone and tri-n-butyl phosphate in vol/vol with increasing mole fractions of DMSO were prepared. The range of mole-fractions are presented in Table 2. Seven mixtures in each system of different mole-fractions were prepared by changing the proportions of the component liquids taking volume and studies were made on these binary solutions. The ultrasonic velocity, density and viscosity of pure liquids such as DMSO, isobutyl methyl ketone, acetyl acetone and tri-n-butyl phosphate were also measured.

Theoretical Aspects

From the measured ultrasonic velocity and density, the isentropic compressibility β_s of a solution is determined by using the relation[21]

$$\beta_s = \frac{1}{\rho C^2} \tag{1}$$

Table 2 Experimentally determined ultrasonic velocity and density (C and ρ) and calculated values of isentropic compressibility, intermolecular free-length, acoustic impedance and viscosity (β_s, L_f, Z and η) of binary mixtures of DMSO and component (2) at 303.15 K.

Mole fraction of DMSO (f_1) (1)	$\rho \times 10^{-3}$ $kg\ m^{-3}$ (2)	$C\ ms^{-1}$ (3)	$\beta_s \times 10^{12}$ m^2N^{-1} (4)	$Z \times 10^{-5}$ $kg\ m^{-2}s^{-1}$ (5)	$L_f \times 10^{10}$ m (6)	$\eta \times 10^{2}$ $Ns\ m^{-2}$ (7)
DMSO(1) + Isobutyl methyl ketone						
0.0000	0.7913	1180.0	907.60	9.337	0.6025	0.5114
0.1332	0.8274	1224.7	805.73	10.133	0.5677	0.6376
0.2570	0.8569	1247.5	749.87	10.689	0.5476	0.7283
0.3722	0.8842	1287.6	682.16	11.384	0.5223	0.8149
0.4798	0.9202	1310.5	632.76	12.054	0.5030	0.9229
0.5804	0.9528	1342.0	582.76	12.786	0.4828	1.0420
0.6748	0.9766	1360.0	553.61	13.281	0.4705	1.1602
0.7635	1.0030	1397.6	510.42	14.017	0.4518	1.3060
1.0000	1.0949	1490.8	410.90	16.323	0.4054	1.8542
DMSO(1) + HAA(2)						
0.0000	0.9661	1293.0	619.00	12.490	0.4980	0.7020
0.1118	0.9816	1329.3	576.52	13.048	0.4802	0.8190
0.2207	0.9954	1364.3	539.73	13.580	0.4646	0.9187
0.3269	1.0070	1380.5	521.07	13.901	0.4565	1.0325
0.4303	1.0190	1406.5	496.07	14.332	0.4454	1.1172
0.5312	1.0330	1427.0	475.39	14.740	0.4360	1.2091
0.6296	1.0440	1439.0	462.57	15.023	0.4301	1.3021
0.7256	1.0570	1453.6	447.74	15.364	0.4232	1.4271
1.0000	1.0949	1490.8	410.90	16.323	0.4054	1.8542
DMSO(1) + TBP(2)						
0.0000	0.9700	1240.0	670.47	12.028	0.5179	2.8170
0.1114	0.9832	1278.3	622.43	12.568	0.4989	3.1479
0.2201	0.9957	1291.5	602.11	12.859	0.4907	2.9624
0.3260	1.0070	1317.3	572.27	13.265	0.4784	2.7991
0.4293	1.0190	1356.0	533.71	13.817	0.4620	2.6541
0.5302	1.0320	1376.3	511.55	14.203	0.4523	2.5817
0.6286	1.0450	1404.0	485.45	14.671	0.4406	2.4206
0.7248	1.0570	1424.7	466.09	15.059	0.4317	2.2906
1.0000	1.0949	1490.8	410.90	16.323	0.4054	1.8542

where, C is the ultrasonic velocity and ρ is the density of the mixture solution. The ultrasonic velocity is also influenced by the acoustic-impedance Z, given by[22]

$$Z = \rho C \tag{2}$$

The intermolecular free-length L_f is the distance covered by a sound wave between the surfaces of the neighbouring molecules, and is given by Jacobson[23] as

$$L_f = k\,\beta_s^{1/2} \tag{3}$$

where k is the temperature dependent constant.

The viscosity of a liquid is based on Poiseuille's formulae

$$\eta = k' T \rho \tag{4}$$

where η is the coefficient of viscosity, T is the time flow of the liquid for emptying the reservoir between the upper and the lower marks of the viscometer and K' is the instrument constant. Excess properties such as $C^E, \beta_s^E, L_f^E, Z^E$ and η^E have been calculated by using the general equation

$$A^E = A_{\text{mixture}} - (f_1 A_1 + f_2 A_2) \tag{5}$$

where A_1 is the parameter $(C, \beta_s, L_f, Z, \eta)$ for DMSO and A_2 is the same parameter for other component, f_1 and f_2 are the mole fractions of DMSO and other component respectively. All excess properties were fitted to a Redlich-Kister type equation:

$$Y^E = f_1 f_2 \sum_{j=1}^{N} A_{j-1}(2f_1 - 1)^{j-1} \tag{6}$$

and the parameter A_{j-1} were computed on a least square fit with the help of IBM PC computer.

RESULTS AND DISCUSSION

The measured values of ρ and C and the calculated values of β_s, Z, L_f and η of binary mixtures of IBMK, HAA and TBP with different mole fractions of DMSO are presented in Table 2 and their corresponding excess properties such as $\beta_s^E, Z^E, L_f^E, C^E$ and η^E at 303.15 K are graphically represented (Figs. 1–5). The non-linear decrease or increase of C, β_s, L_f and η values with the change in composition of the mixture in each system indicates the presence of molecular interaction[24]. The constants of Eqn. (6), viz., A_0 to A_3 computed for $\beta_s^E, Z^E, L_f^E, C^E$ and η^E determined by least square fit method along with the standard deviations σ are given in Tables 3, 4 and 5 at 303.15 K.

The excess properties β_s^E and L_f^E are entirely negative for all the systems i.e. DMSO + IBMK, DMSO + HAA and DMSO + TBP. The minima of this

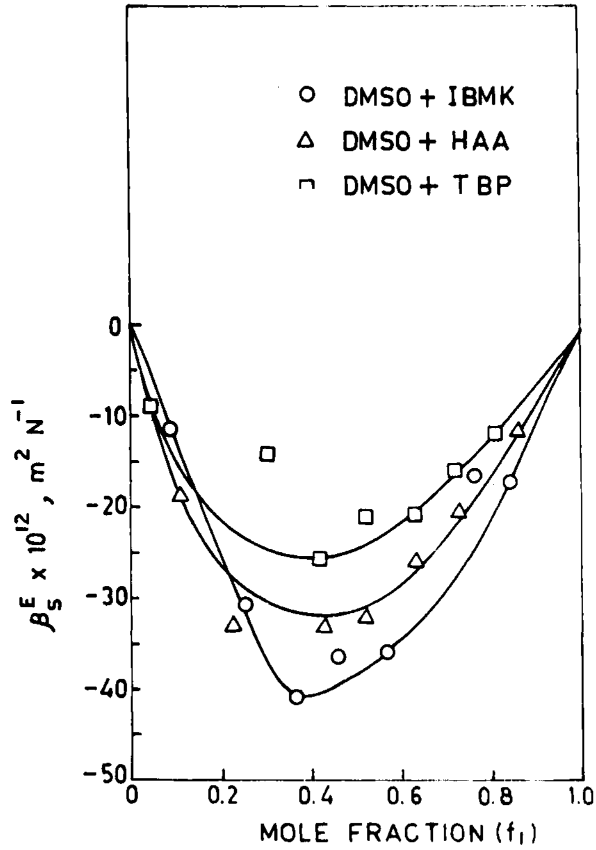

Figure 1 Plot of excess isentropic compressibility (β_s^E) vs. mole fraction of DMSO.

Table 3 Coefficients $\times 10^{12}$ of Eqn. (6) for excess isentropic compressibility (β_s^E) in $m^2 N^{-1}$.

System	A_0	A_1	A_2	A_3	$\sigma \times 10^{12}$ ($m^2 N^{-1}$)
DMSO + IBMK	−145.30	−77.80	240.4	87.04	10.490
DMSO + HAA	−136.40	−50.92	218.6	60.16	9.081
DMSO + TBP	−93.18	−53.11	133.0	14.54	7.680

Table 4 Coefficients $\times 10^3$ of Eqn. (6) for excess viscosity (η^E) in Ns m^{-2}.

System	A_0	A_1	A_2	A_3	$\sigma \times 10^3$ ($Ns\, m^{-2}$)
DMSO + IBMK	−0.954	−0.980	0.844	0.020	0.096
DMSO + HAA	−0.387	−0.543	0.070	0.018	0.056
DMSO + TBP	1.137	0.385	−0.176	−0.621	0.077

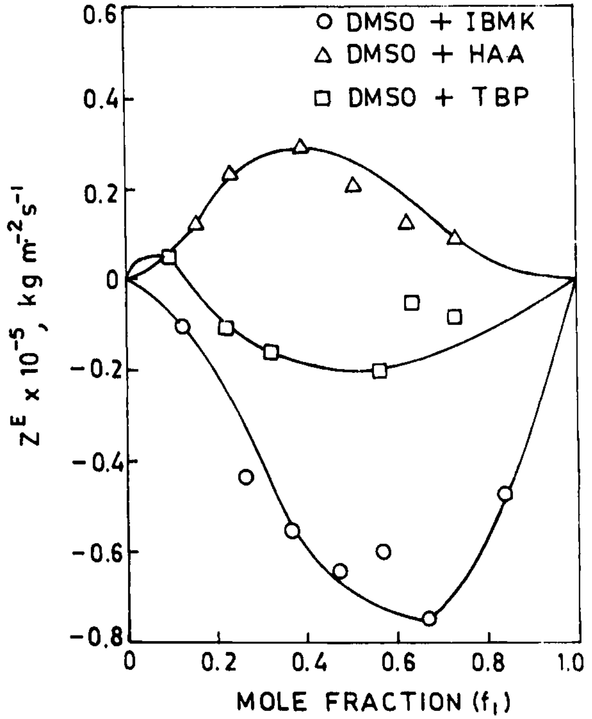

Figure 2 Plot of excess acoustic impedance (Z^E) vs. mole fraction of DMSO.

Table 5 Coefficients $\times 10^{-5}$ of Eqn. (6) for excess ascoustic impedance (Z^E) in kg m^{-2} s^{-1}.

System	A_0	A_1	A_2	A_3	$\sigma \times 10^{-5}$ ($kg\ m^{-2} s^{-1}$)
DMSO + IBMK	−0.0179	−0.0040	0.0383	0.0171	0.0017
DMSO + HAA	−0.0503	−0.0169	0.0837	0.0198	0.0032
DMSO + TBP	−0.0258	−0.0150	0.0388	0.0007	0.0023

Table 6 Coefficients $\times 10^{10}$ of Eqn. (6) for excess intermolecular free length (L_f) in m.

System	A_0	A_1	A_2	A_3	$\sigma \times 10^{10}$ *(m)*
DMSO + IBMK	−0.0179	−0.0040	0.0383	0.0171	0.0017
DMSO + HAA	−0.0503	−0.0169	0.0837	0.0198	0.0032
DMSO + TBP	−0.0258	−0.0150	0.0388	0.0007	0.0023

parameter occurs at about 0.37 mole-fraction of DMSO. Fort and Moore[25] and others[26,27] have suggested that the excess isentropic compressibility becomes increasingly negative with the increasing strength of interaction between the component liquids. This may be due to dipole-induced dipole and dipole-dipole interaction between component molecules.

Table 7 Coefficients of Eqn. (6) for excess ultrasonic velocity in ms^{-1}.

System	A_0	A_1	A_2	A_3	$\sigma(ms^{-1})$
DMSO + IBMK	−71.26	−103.6	20.89	−33.97	11.250
DMSO + HAA	111.30	71.92	−140.60	−71.75	9.095
DMSO + TBP	17.47	14.29	−32.75	22.29	3.835

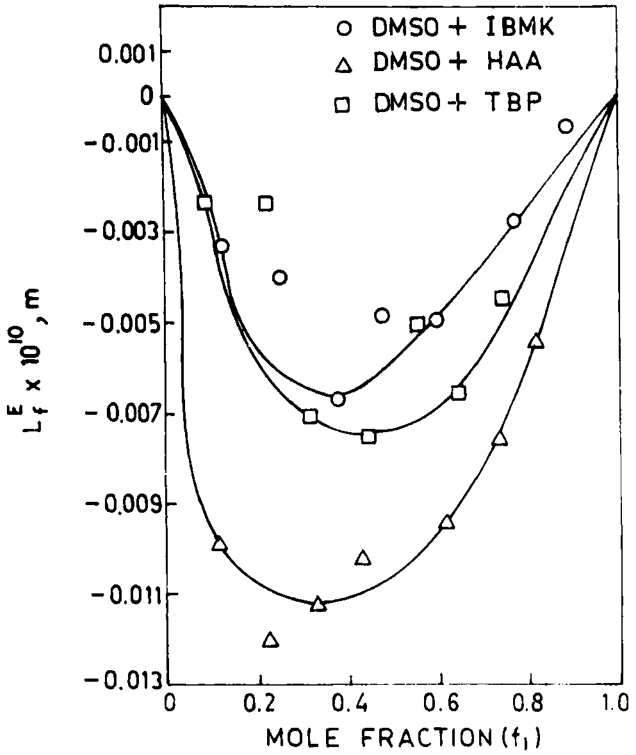

Figure 3 Plot of excess intermolecular free length (L_f^E) vs. mole fraction of DMSO.

The η^E values for DMSO + IBMK and DMSO + HAA are entirely negative and for DMSO + TBP are entirely positive for all mole-fractions of DMSO. The negative values of η^E indicates that dispersion forces and dipolar forces are operating between unlike molecules of binary mixtures. Shah *et al.*[28] have suggested that the greater positive value of η^E leads to stronger molecules interactions in binary liquid mixtures. Positive values of η^E for DMSO + TBP mixture suggest that specific interactions leading to complex formation are likely to operate between the components[29,30]. This may be due to the dipole-induced-dipole interactions between unlike molecules. The large and bulky acetyl and isobutyl groups will increase loose packing in the mixtures. Therefore available free volume in the

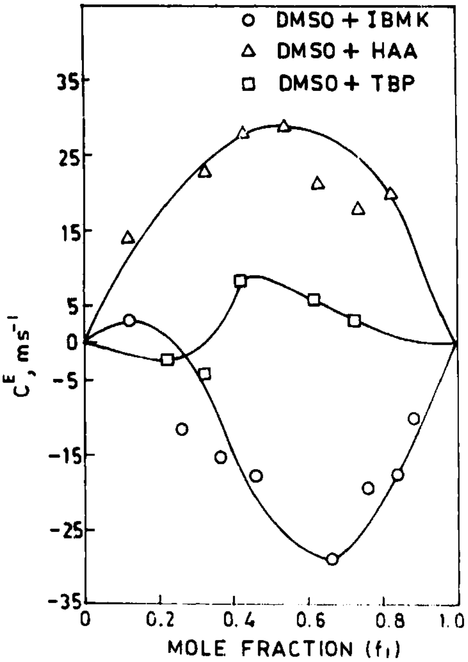

Figure 4 Plot of excess ultrasonic velocity (C^E) vs. mole fraction of DMSO.

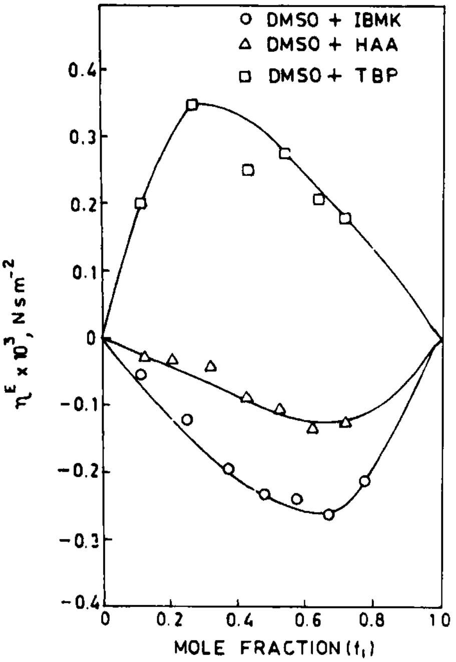

Figure 5 Plot of excess viscosity (η^E) vs. mole fraction of DMSO.

mixture will be more and hence, the interaction between unlike molecules decreases. The Z^E values are positive for DMSO + HAA system and are negative for DMSO + IBMK system and DMSO + TBP systems. The positive values indicates stronger molecular interaction between unlike molecules. The C^E values for DMSO + HAA systems are entirely positive, C^E value is entirely negative for DMSO + IBMK and is almost positive for DMSO + TBP. C^E value is more positive at 0.5 mole fraction of DMSO for DMSO + HAA system. Piotrowska and Kaulgud[26,27] have established that the negative values of excess functions are indication of complex formation between the component liquids of the mixture solution and are influenced by their interactions.

From these experimental results, greater negative values of η^E, β_s^E, L_f^E and greater positive values of Z^E and C^E for DMSO + HAA system suggests that stronger molecular interaction is likely to operate between the unlike molecules than other two mixtures. This enhanced interaction may be due to dipole induced dipole interaction. The results of the present study show the applicability of various excess thermodynamic parameters as a potential probe to investigate the molecular interactions in binary liquid mixtures.

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