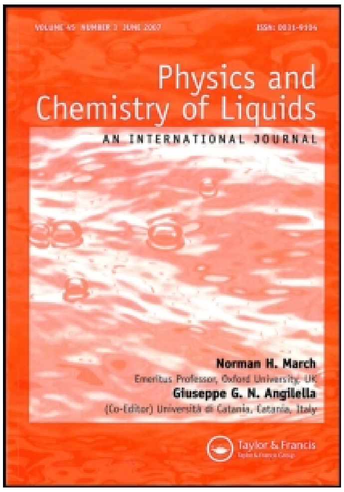

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THERMODYNAMIC INTERACTIONS IN BINARY MIXTURES OF DIMETHYL SULPHOXIDE WITH AMINES FROM THE EXCESS PROPERTIES OF ULTRASONIC VELOCITY, VISCOSITY AND DENSITY

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Experimental values of density, viscosity and ultrasonic velocity are presented for the binary mixtures of dimethyl sulphoxide (DMSO) with methyl amine (CH_3NH_2), dimethyl amine ($(CH_3)_2NH$) and trimethyl amine ($(CH_3)_3N$) at 303.15 K over the entire mole fraction of the mixture components. From these data, excess isentropic compressibility (β_S^E), excess intermolecular free-length (L_f^E), excess acoustic impedance (Z^E), excess viscosity (η^E) and excess volume (V^E) have been calculated. These quantities are further fitted to the Redlich-Kister relation to estimate the binary interaction parameters and standard errors. The results are analysed in terms of nature and degree of interaction between the component molecules. The nature of variation of these excess parameters provides information about the type of interaction taking place in these binary systems.

Keywords: Ultrasonic velocity; viscosity; acoustic impedance; intermolecular free-length

1. INTRODUCTION

The knowledge of thermodynamic and physico-chemical properties of liquid mixtures of two or more components are of considerable theoretical and industrial importance due to their wide range of applicability as solvent media in various physico-chemical processes.

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Dimethyl sulphoxide (DMSO) is a versatile dipolar aprotic solvent (having a dielectric constant $\varepsilon = 46.50$) used extensively in kinetic studies and electrochemistry and as a solvent for polymers. Binary mixtures of DMSO with aliphatic and aromatic solvents are of interest in studies of polymer miscibility, polymer phase diagrams and preferential interaction of polymers in mixed solvents [1–4]. Considerable work has been carried out by Letcher and Rao [5, 6] on excess volumes of mixing of primary, secondary and tertiary amines with hydrocarbons and DMSO but no data is reported on thermodynamic interactions of binary mixtures containing DMSO with aliphatic amines. Ultrasonic studies of many commercial extractants with various diluents have been made in order to understand molecular interactions. It is an important parameter being frequently used to investigate the intermolecular interactions in the binary liquid mixtures [7–11]. In continuation of the earlier work [12–14] in this laboratory on molecular interactions, we report in the present paper excess isentropic compressibility (β_s^E), excess intermolecular free-length (L_f^E), excess acoustic impedance (z^E), excess molar volume (V^E) and excess viscosity (η^E) from ultrasonic velocity, viscosity and density measurements of binary mixtures of methyl amine, dimethyl amine and trimethyl amine with dimethyl sulphoxide at 303.15 K in order to understand molecular interactions.

2. MATERIALS AND METHODS

Dimethyl sulphoxide used was 99.5 % pure and was further purified by the methods described by Gopal *et al.* [15]. All amines were dried over potassium hydroxide pellets for several days. They were then distilled using a vacuum jacket column packed with a pyrex glass rings. All the chemicals used were of analytical grade (E. Merk and BDH). The purity of the samples was checked by comparing the measured densities with those reported in literature [16–18].

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 double 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}).

Binary mixtures of DMSO with methyl amine, dimethyl amine and trimethyl amine in vol/vol with increasing molefractions of DMSO were prepared. The range of molefractions are presented in Table II. Six mixtures in each system of different molefraction 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, methyl amines, dimethyl amine and trimethyl amine were also measured.

3. THEORETICAL ASPECTS

From the measured ultrasonic velocity and density, the isentropic compressibility β_s of a solution is determined by using the relation [19],

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

TABLE I Densities of pure components

Compound	*Density, g cm*$^{-3}$ *Experimental*	(303.15 K) *Literature*
Dimethyl sulphoxide	1.0949	1.0958
Methyl amine	0.8916	0.6628 (293 K)
Dimethyl amine	0.8856	0.6501 (298 K)
Trimethyl amine	0.9978	0.6287 (298 K)

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

Mole fraction of DMSO (f_1)	ρ $kg\ m^{-3}$	C mS^{-1}	$\beta \times 10^{12}$ m^2N^{-1}	$Z \times 10^{-5}$ $kg\ m^{-2}S^{-1}$	$L_f \times 10^{10}$ m	$V \times 10^6$ $m^3\ \mathrm{mol}^{-1}$	$\eta \times 10^3$ $Ns\ m^{-2}$
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
			DMSO(1) + CH_3NH_2(2)				
0.0607	906.20	1669	396.15	15.124	0.3980	37.427	1.738
0.1200	921.33	1678	385.47	15.460	0.3926	39.842	1.823
0.2348	943.14	1691	370.79	15.948	0.3851	44.650	1.891
0.4501	990.70	1708	346.00	16.921	0.3720	52.736	2.172
0.6481	1019.40	1685	345.50	17.176	0.3717	60.394	2.077
0.8308	1054.90	1610	365.71	16.983	0.3824	66.514	1.895
			DMSO + $(CH_3)_2NH$				
0.0610	904.90	1569.5	448.61	14.202	0.4236	52.047	2.067
0.1207	918.00	1584.5	433.88	14.545	0.4165	53.452	2.133
0.2361	939.70	1587.0	422.52	14.913	0.4111	56.276	2.207
0.4518	981.04	1590.0	403.19	15.598	0.4015	61.171	2.373
0.6496	1015.40	1575.0	397.01	15.992	0.3985	65.539	2.207
0.8318	1052.20	1548.0	396.60	16.288	0.3982	68.970	1.939
			DMSO + $(CH_3)_3N$				
0.0546	1003.0	1569.0	404.99	15.737	0.4024	59.968	0.8704
0.1086	1010.2	1574.0	399.56	15.900	0.3997	60.557	0.9640
0.2152	1023.5	1599.6	381.81	16.372	0.3907	61.751	1.1748
0.4224	1049.0	1619.0	363.68	16.983	0.3814	64.007	1.8035
0.6220	1078.0	1629.0	349.57	17.560	0.3739	65.807	2.6220
0.8144	1090.5	1601.5	357.53	17.464	0.3781	68.408	2.6102

For pure DMSO, the measured and calculated data are
$\rho = 1.0949\ \mathrm{g\ cm^{-3}}$, $C = 1490.88\ \mathrm{mS^{-1}}$, $\eta = 1.8542 \times 10^{-3}\ \mathrm{Ns\ m^{-2}}$
$Z = 16.323 \times 10^{-5}\ \mathrm{kg\ m^{-2}\ S^{-1}}$, $\beta_S = 410.90 \times 10^{-12}\ \mathrm{m^2\ N^{-1}}$, $L_f = 0.4054 \times 10^{-10}$ m.

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 [20]

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

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 [21] 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 of flow of the liquid for emptying the reservoir between the upper and lower marks of the viscometer and k' is the instrument constant.

Excess properties such as V^E, β_s^E, L_f^E, Z^E and η^E have been calculated by using the general equation

$$A^E = A_{\text{mixture}} - (f_1A_1 + f_2A_2) \tag{5}$$

where A_1 is the parameter (V, β_s, Z, L_f, η) for DMSO and A_2 is the same parameter for amines, f_1 and f_2 are the mole-fraction of DMSO and amines, respectively.

All excess properties were fitted to a Redlich-Kister type equation:

$$Y^E = f_1f_2\sum_{j=1}^{N} A_{j-1}(2f_1 - 1)^{j-1} \tag{6}$$

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

4. RESULTS AND DISCUSSION

The measured values of ρ and C and the calculated values of β_s, L_f and η of the binary mixtures of methyl amine, dimethyl amine and trimethyl amine with different molefractions of DMSO are presented in Table-II and their corresponding excess properties such as $\beta_s^E, L_f^E, Z^E, V^E$ 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 indicate the presence of molecular interaction [22]. The constants of equation (6), viz., A_o to A_3 computed for $\beta_s^E, Z^E, L_f^E, V^E$ and η^E determined by least square fit method along with the standard deviation σ are given in Tables III, IV, V, VI and VII at 303.15 K. Non linear dependence of the various thermodynamic parameters and the excess functions like $\beta_s^E, V^E, L_f^E, Z^E$ and η^E as a function of solvent

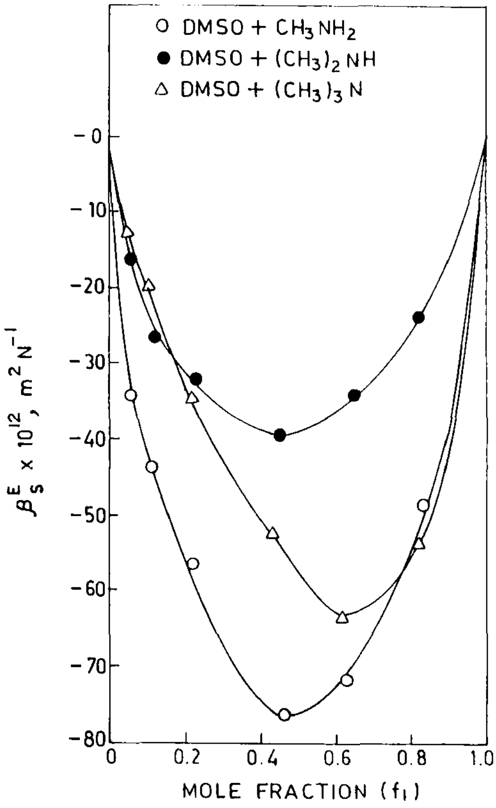


FIGURE 1 Plot of excess isentropic compressibility (β_s^E) vs. molefraction of DMSO.

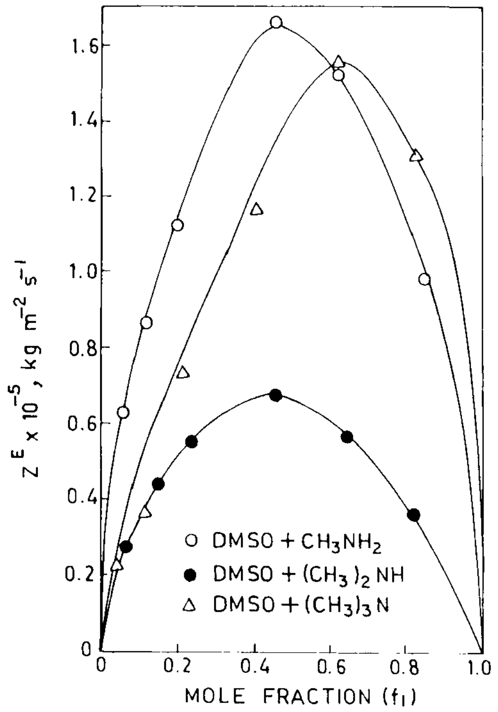


FIGURE 2 Plot of excess acoustic impedance (Z^E) vs. molefraction of DMSO.

composition is attributed to the existence of dipolar interaction between the solvent components in binary mixtures.

The excess properties β_s^E and L_f^E of DMSO+ amines are all negative throughout the whole range of composition of the mixture. β_s^E and L_f^E for DMSO + CH_3NH_2 and DMSO + $(CH_2)_3NH$ systems attain a minimum value at about 0.45 mole fraction of DMSO. The Z^E values are maximum positive for DMSO + CH_3NH_2 system and Z^E attains a maximum value at about 0.45 mole fraction of DMSO. The V^E values for DMSO + CH_3NH_2 system and DMSO + $(CH_3)_2NH$ system are entirely positive and V^E is entirely negative for DMSO + $(CH_3)_3N$ system in the whole range of composition of the mixture. V^E value is more + ve at 0.62 mole fraction of DMSO + CH_3NH_2 system. η^E values for all the systems are positive. The maximum η^E value shifting towards higher mole fraction of

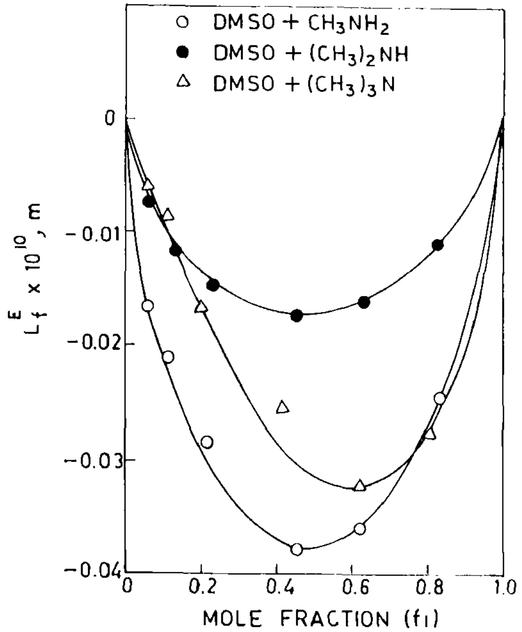


FIGURE 3 Plot of excess intermolecular free length (L_f^E) vs. mole-fraction of DMSO.

DMSO is in the order of DMSO + $(CH_3)_2NH$ < DMSO + CH_3NH_2 < DMSO + $(CH_3)_3N$.

The above findings are in agreement with Fort and Moore [23] Piotrowska [24] and Kaulgud [25] 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. The observed V^E may be discussed in terms of several effects which may be arbitrarily divided into physical, chemical and geometrical contributions. The physical interactions involve mainly dispersion forces giving a positive contribution. The chemical or specific interactions result in a volume decrease and these include charge transfer type forces i.e. forming and/or breaking of H-bonds and other complex forming interaction. Structural contributions arising from the geometrical fitting of one component into the other due to difference in molar volume and free volume between components, lead to − ve contributions to V^E. According to

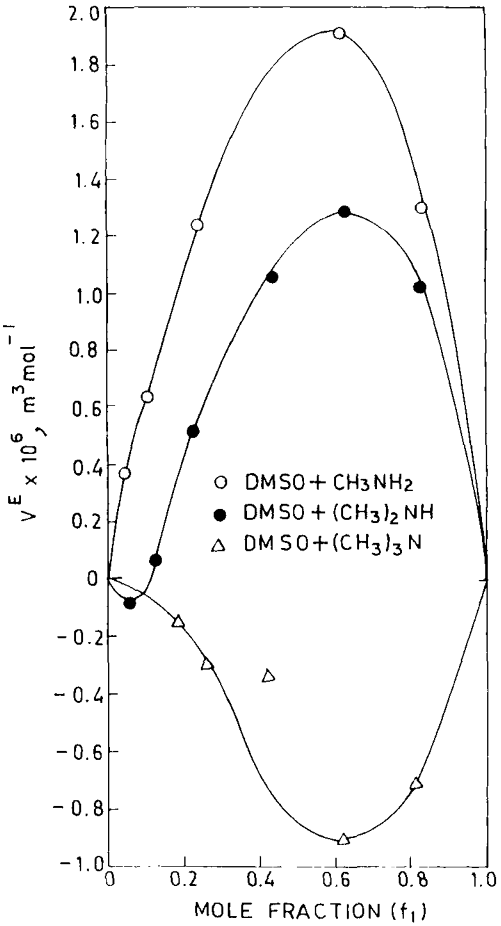


FIGURE 4 Plot of excess volume (V^E) vs. mole-fraction of DMSO.

Krishnaiah and other [26] the actual value of V^E depends on the balance between two opposing contributions i.e. (i) loss of dipolar association (ii) dipole–dipole, dipole induced dipole interactions and charge transfer complexation between unlike molecules.

The values of β_s may be interpreted in terms of effects due to mutual dissociation of molecules and the formation of hydrogen bonds between unlike molecules. The former effect contributes to an expansion in volume and hence the mixture becomes more compressible,

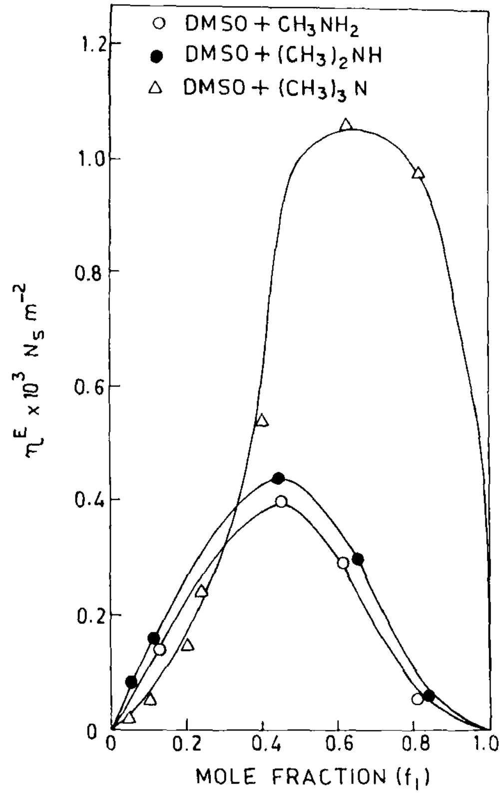


FIGURE 5 Plot of excess viscosity (η^E) vs. mole-fraction of DMSO.

TABLE III Coefficients $\times 10^{12}$ of Eq. (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 + CH_3NH_2	−296.6	33.37	−178.8	−60.58	4.906
DMSO + $(CH_3)_2NH$	−148.1	38.18	−110.0	−16.38	1.645
DMSO + $(CH_3)_3N$	−230.5	−131.70	−124.8	−0.07	1.121

TABLE IV Coefficients × 10^3 of Eq. (6) for excess viscosity (η^E) is Ns m^{-2}

System	A_0	A_1	A_2	A_3	$\eta \times 10^3$ (Ns m^{-2})
DMSO + CH_3NH_2	1.569	−0.5492	−1.588	0.2616	0.0294
DMSO + $(CH_3)_2NH$	1.689	−0.8304	−1.514	0.2604	0.0226
DMSO + $(CH_3)_3N$	3.273	4.4100	−1.244	0.7564	0.0544

TABLE V Coefficient × 10^{-5} of Eq. (6) for excess acoustic impedance (Z^E) in kg m^{-2} s^{-1}

System	A_0	A_1	A_2	A_3	$\eta \times 10^{-5}$ *(kg m* $^{-2}S^{-1}$*)*
DMSO + CH_3NH_2	6.472	−0.4908	2.215	1.127	0.0969
DMSO + $(CH_3)_2NH$	2.549	−0.8087	1.875	0.314	0.0334
DMSO + $(CH_3)_3N$	5.451	3.6450	2.462	0.187	0.0299

TABLE VI Coefficients × 10^{10} of Eq. (6) for excess intermolecular free length (L_f^E) in m

System	A_0	A_1	A_2	A_3	$\eta \times 10^{10}$ *(m)*
DMSO + CH_3NH_2	−0.1517	0.0170	−0.0784	−0.0325	0.0025
DMSO + $(CH_3)_2NH$	−0.0709	0.0185	−0.0454	−0.0072	0.0007

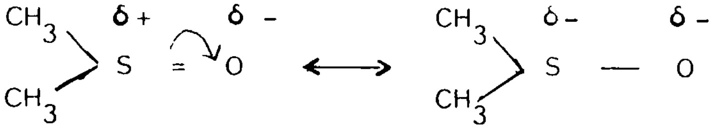
TABLE VII Coefficients × 10^6 of Eq. (6) for excess molar volume (V^E) in m^3 mol^{-1}

System	A_0	A_1	A_2	A_3	$\eta \times 10^6$ (m^3 mol^{-1})
DMSO + CH_3NH_2	6.680	2.598	3.337	0.241	0.084
DMSO + $(CH_3)_2NH$	4.781	4.627	−0.857	−0.876	0.076

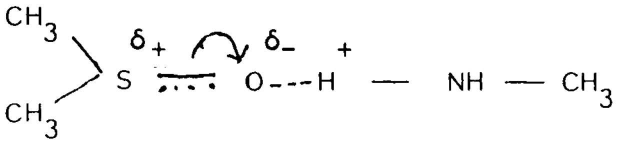
while the latter effect is responsible for a contraction in volume and hence the compressibility of the mixture is less than that of pure components.

The sign and magnitude of V^E and β_S^E depends on the strength of hydrogen bonding of amines in their pure state and in mixture. In branched amines the presence of methyl groups on the α-carbon atom controls the hydrogen bond strength. These methyl groups increases the electron density at the oxygen atom and increase the association due to the electromeric effect. Further the presence of methyl groups also decrease the association due to steric effect. A result of the above two effects may be related to the order observed in β_s^E.

Shah *et al.* [27] have suggested that the greater positive values of η^E lead to stronger molecular interactions in binary liquid mixtures. Positive η^E values indicate strong hydrogen bonding. Liler and Kosanovic [28] and others [29, 30] have discussed the shapes of plots of η against mole fraction for binary liquid mixtures in terms of complex formation and the maxima are said to indicate the formation of stable complexes. Negative values of L_f^E which indicates hydrogen bonding may be due to complexation between unlike molecules through charge transfer interactions. This may be explained by considering the presence of polar sulphoxide group due to resonance in DMSO molecule.



The dipoles in Amines and DMSO arise due to differences in electronegativities of nitrogen, oxygen and hydrogen. Following type of dipole–dipole associations arising from the fractional negative charge on oxygen of DMSO molecule and fractional + ve charge on H atom of Amine may be proposed.



Positive values of Z^E indicates stronger molecular interaction between unlike molecules. The variation of ultrasonic velocity in a solution depends upon the increase or decrease of intermolecular free length after mixing the components. On the basis of a model for sound propagation proposed by Eyring and Kincaid [31] and others [32], ultrasonic velocity should increase if the intermolecular free length decreases as a result of mixing of components. This behaviour indicates significant interaction between DMSO and amine molecules.

In the binary systems of present study, methyl amine interacts more strongly with DMSO than other two mixtures. But the experimental findings indicate that specific type of interaction is also operating between the other two mixtures. It may therefore be concluded that the resultant interaction in a binary mixture is not solely dependent on the molecular structure of the component liquids but also influenced by other factors like dispersion forces, dipole–dipole interaction, hydrogen bonding, charge transfer interaction and/or complex formation. However it was observed from these studies that the polarity of the component liquids play a very significant role in determining the strength of molecular interaction in a binary mixture.

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