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The densities, ρ, ultrasonic speeds, u and viscosities, η of binary mixtures of dimethylsulphoxide (DMSO) with cyclohexanol, cyclohexanone and cyclohexylamine, with DMSO as a common component, over the whole composition range expressed by mole fraction of DMSO, including those of pure liquids have been measured at 30°C. By using the experimental values of ρ, u and η, the deviations in isentropic compressibility, Δk_s, excess intermolecular free length, L_f^E, excess molar volume, V^E, deviations in viscosity, $\Delta\eta$, excess free energy of activation of viscous flow, G^{*E}, partial molar compressibility and volume, $\bar{K}_{\phi,2}^o$ and $\bar{V}_{\phi,2}^o$ respectively of cyclohexanol/ cyclohexanone/cyclohexylamine in DMSO at infinite dilution have been calculated. The variations of these parameters with composition of the mixture suggest that the strength of interactions in these mixtures follow the order: cyclohexanol < cyclohexanone < cyclohexylamine. The isothermal compressibility, k_T for these binary mixtures has been theoretically calculated by using the Flory's statistical theory and five hard sphere models and the results were compared with the experimental k_T values. Further, the viscosities of these binary mixtures were theoretically predicted on the basis of various relations by using the experimental values of pure components and the results were compared with the experimental findings.

Keywords: Density; Ultrasonic speed; Viscosity; Binary mixtures; Isothermal compressibility

1. Introduction

The knowledge of physicochemical properties of non-aqueous binary liquid mixtures has relevance in theoretical and applied areas of research, and such results are frequently used in design process (flow, mass transfer or heat transfer calculations) in many chemical and industrial processes. The excess properties derived from these physical property data reflect the physicochemical behaviour of the liquid mixtures with respect to the solution structure and intermolecular interactions between the component molecules of the mixture. As a part of our studies [1–5] on the acoustics, volumetric and

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transport properties of non-aqueous binary liquid mixtures, we report here the results of our study on binary mixtures of dimethylsulphoxide (DMSO) with cyclohexanol, cyclohexanone and cyclohexylamine. DMSO is a versatile compound having wide range of applicability as solvent in chemical as well as biological processes involving both plants and animals [6,7]. It is highly polar ($\mu = 3.96$ D) [8] and strongly associated aprotic solvent due to S=O group in the molecule [9]. In the pure state, DMSO molecules associate to form chains with parallel dipole moments, while the neighbouring DMSO molecules from the adjacent chains are oriented with anti-parallel dipole moments [10,11], as reported by Bertagnolli *et al.* [10] using X-ray and neutron scattering; and confirmed by Vaisman and Berkowitz [11] using molecular dynamics simulation. Cyclohexanol, cyclohexanone and cyclohexylamine are also polar ($\mu = 1.86$, 2.87 and 1.3 D) [8] and cyclohexanol is highly associated [9], whereas cyclohexylamine is associated [9] and cyclohexanone is unassociated [9]. These liquids are used in production of adipic acid (nylon intermediate), as industrial solvents (as antioxidants, vulcanization accelerators, anticorrosive, etc.), and cyclohexanol is used in production of soaps and detergents, and intermediate for plasticizers, pharmaceuticals, pesticides, etc. Moreover, literature survey indicates that no physicochemical study on these systems has been reported. Therefore, the study of intermolecular interactions in these systems will be interesting owing to their applications.

This work reports the densities, ρ, ultrasonic speeds, u and viscosities, η of binary mixtures of DMSO with cyclohexanol, cyclohexanone and cyclohexylamine, including pure liquids, over the whole composition range at 30°C. Using these experimental values of ρ, u and η, the excess functions such as Δk_s, L_f^E, V^E, $\Delta \eta$ and G^{*E}, apparent molar compressibility and volume, $K_{\phi,2}$ and $V_{\phi,2}$, and partial molar compressibility and volume, $\bar{K}_{\phi,2}^o$ and $\bar{V}_{\phi,2}^o$ of cyclohexanol/cyclohexanone/cyclohexylamine in DMSO at infinite dilution have been calculated. The dependence of these parameters on composition has been used to explain the nature and extent of intermolecular interactions in these mixtures.

The isothermal compressibility, k_T and η of these binary mixtures were theoretically calculated in terms of pure component data by using Flory's theory, hard sphere models and different viscosity relations, and the results were compared with experimental findings.

2. Experimental

DMSO (E. Merck, Germany, purity >99.5%), cyclohexanol, cyclohexanone and cyclohexylamine (all SD Fine Chemicals, India, analytical reagent grade) were purified by using the methods described in the literature [12,13]. Before use, all the liquids were stored over 0.4 nm molecular sieves to reduce water content, if any, and were degassed. The mixtures were prepared by mass in a dry box and were kept in special airtight bottles. The weighings were performed on Precisa XB-220A (Swiss make) electronic balance with a precision of ± 0.1 mg.

The densities of pure liquids and their binary mixtures were measured by using a single-capillary pycnometer (made of Borosil glass) having a bulb capacity of 8×10^{-6} m^3, as described in our earlier works [1–6]. The accuracy in the density measurements was found to be ± 0.1 kg m^{-3}. The ultrasonic speeds in pure liquids and in their mixtures were measured using a single-crystal variable-path ultrasonic

interferometer operating at 3 MHz with an accuracy of ±0.05%. The viscosities of pure liquids and their binary mixtures were measured by using Ubbelohde-type suspended level viscometer as described in our previous works [1–6]. The accuracy in the viscosity measurements was within $\pm 1 \times 10^{-6}\,\mathrm{N\,s\,m^{-2}}$. The temperature of the test liquids during the measurements was maintained to an accuracy of ±0.02°C in an electronically controlled (JULABO, Model-MD, Germany) thermostated water bath.

The reliability of the experimental data (ρ, u and η) has been checked by comparing the observed values of these properties of pure liquids with the corresponding literature values, which were available for these liquids at 30°C. For example, the observed values of ρ for pure DMSO, cyclohexanol and cyclohexanone at 30°C are 1.0910, 0.9418 and $0.9375\,\mathrm{g\,cm^{-3}}$, respectively (literature values: 1.0911 [14]/1.0910 [15], 0.9416 [8] and $0.9374\,\mathrm{g\,cm^{-3}}$ [16]); the observed value of u for DMSO at 30°C is $1470.5\,\mathrm{m\,s^{-1}}$ (literature value: 1474.0 [14]/$1470.4\,\mathrm{m\,s^{-1}}$ [4]) and observed values of η for DMSO and cyclohexanone at 30°C are 1.7944 and 1.7984 cP, respectively (literature values: 1.79 [15]/1.7984[4] and 1.799 cP [16]).

3. Results and discussion

The experimental values of ρ, u and η of pure DMSO, with cyclohexanol/cyclohexanone/cyclohexylamine and their twenty-seven binary mixtures over the whole composition range expressed by mole fraction, x_1 of DMSO at 30°C are listed in table 1. From these experimental values of ρ, u and η, the excess functions such as Δk_s, L_f^E, V^E, $\Delta \eta$ and G^{*E} were calculated by using the following relations:

$$\Delta k_s = k_s - (\phi_1 k_{s1} + \phi_2 k_{s2}) \tag{1}$$

$$L_f^E = L_f - (x_1 L_{f1} + x_2 L_{f2}) \tag{2}$$

$$V^E = x_1 M_1 (1/\rho - 1/\rho_1) + x_2 M_2 (1/\rho - 1/\rho_2) \tag{3}$$

$$\Delta \eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \tag{4}$$

$$G^{*E} = RT[\ln(\eta V) - x_1 \ln(\eta_1 V_1) - x_2 \ln(\eta_2 V_2)] \tag{5}$$

where M is the molar mass; R is the universal gas constant; T is the absolute temperature; the subscripts 1 and 2 stand for pure components, DMSO and cyclohexanol/cyclohexanone/cyclohexylamine, respectively; k_s, L_f and V are the isentropic compressibility, intermolecular free length and molar volume, respectively, and were evaluated by using the following relations.

$$k_s = (\rho u^2)^{-1} \tag{6}$$

$$L_f = K'/u\rho^{1/2} \tag{7}$$

$$V = (x_1 M_1 + x_2 M_2)/\rho \tag{8}$$

where K' is a temperature-dependent constant.

The values of Δk_s, L_f^E, V^E, $\Delta \eta$ and G^{*E} of the binary mixtures were fitted to a Redlich–Kister-type [17] polynomial equation

Table 1. Values of densities, ρ, ultrasonic speeds, u and viscosities, η of binary mixtures as a function of mole fraction, x_1 of DMSO at 30°C.

x_1	ρ (kg m^{-3})	u (m s^{-1})	η (10^{-3} N s m^{-2})
DMSO + Cyclohexanol			
0.0000	941.8	1442.6	39.5461
0.1009	951.3	1446.7	20.8312
0.1821	959.5	1449.8	12.4027
0.2727	969.6	1453.0	7.8351
0.3730	981.9	1456.3	5.3862
0.4703	994.9	1459.2	4.0693
0.5678	1009.2	1461.8	3.2655
0.6724	1026.0	1464.4	2.7317
0.7910	1047.0	1467.1	2.2034
0.8922	1067.1	1468.9	2.0154
1.0000	1091.0	1470.5	1.7944
DMSO + Cyclohexanone			
0.0000	937.5	1399.5	1.7984
0.0990	954.0	1407.3	1.7212
0.1791	968.4	1413.7	1.6692
0.2687	983.5	1420.6	1.6488
0.3683	999.0	1428.0	1.6478
0.4653	1014.3	1435.0	1.6572
0.5628	1029.3	1441.8	1.6750
0.6679	1044.9	1448.9	1.6980
0.7877	1062.0	1456.9	1.7246
0.8903	1075.4	1463.6	1.7552
1.0000	1091.0	1470.5	1.7944
DMSO + Cyclohexylamine			
0.0000	859.8	1396.1	1.6484
0.1000	883.4	1404.5	1.5714
0.1807	905.5	1411.1	1.5184
0.2707	928.4	1418.2	1.4811
0.3707	952.1	1425.9	1.4672
0.4679	975.8	1433.2	1.4700
0.5654	998.4	1440.3	1.4966
0.6703	1021.5	1447.8	1.5417
0.7894	1047.5	1456.3	1.6115
0.8913	1067.6	1463.2	1.6923
1.0000	1091.0	1470.5	1.7944

$$Y^E = x_1 x_2 \sum_{i=1}^{5} A_i (1 - 2x_1)^{i-1} \qquad (9)$$

where Y^E is Δk_s or L_f^E or V^E or $\Delta\eta$ or G^{*E}. The coefficients, A_i of the fitting equation (9), evaluated by using least-squares method, along with the standard deviations, $\sigma(Y^E)$ are given in table 2. The variations of Δk_s, L_f^E, V^E, $\Delta\eta$ and G^{*E} with mole fraction, x_1 of DMSO for the binary mixtures are shown graphically in figures 1–5.

The variations of Δk_s and L_f^E represented in figures 1 and 2, respectively, show that the Δk_s and L_f^E values are small positive for DMSO + cyclohexanol mixtures and are negative for DMSO + cyclohexanone/cyclohexylamine mixtures over the whole composition range. The observed positive Δk_s and L_f^E values suggest the presence of weak interaction between DMSO and cyclohexanol molecules in DMSO + cyclohexanol mixture, i.e., DMSO–cyclohexanol interaction is weaker than the DMSO–DMSO or

Table 2. Coefficients, A_i of equation (9) and standard deviations, $\sigma(Y^E)$ for the binary mixtures.

Property	A_1	A_2	A_3	A_4	A_5	$\sigma(Y^E)$
DMSO + Cyclohexanol						
$\Delta k_s\ (10^{-11}\,\mathrm{m^2\,N^{-1}})$	0.9857	−0.1690	0.1907	−0.0793	−0.2517	0.0010
$L_f^E(10^{-11}\mathrm{m})$	0.6649	−0.1125	0.0962	−0.0376	−0.1154	0.0005
$V^E\ (10^{-6}\,\mathrm{m^3\,mol^{-1}})$	0.9575	0.3606	0.3240	−0.2762	−0.3233	0.0025
$\Delta\eta\ (10^{-3}\,\mathrm{N\,s\,m^{-2}})$	−67.2194	−53.4329	−57.1677	−32.3371	3.8488	0.0197
$G^{*E}\ (\mathrm{kJ\,mol^{-1}})$	−8.0464	−0.9130	−2.7487	1.1672	3.8488	0.0197
DMSO + Cyclohexanone						
$\Delta k_s\ (10^{-11}\,\mathrm{m^2\,N^{-1}})$	−3.8158	−0.7605	−0.9306	0.4563	2.4339	0.0051
$L_f^E(10^{-11}\mathrm{m})$	−1.4528	−0.2638	−0.4042	0.1895	1.1205	0.0024
$V^E\ (10^{-6}\,\mathrm{m^3\,mol^{-1}})$	−6.8067	−1.0922	−1.7832	0.3631	4.3208	0.0090
$\Delta\eta\ (10^{-3}\,\mathrm{N\,s\,m^{-2}})$	−0.5276	−0.3976	−0.3732	0.1716	0.3258	0.0004
$G^{*E}\ (\mathrm{kJ\,mol^{-1}})$	−0.7855	−0.6163	−0.5858	0.2912	0.6354	0.0010
DMSO + Cyclohexylamine						
$\Delta k_s\ (10^{-11}\,\mathrm{m^2\,N^{-1}})$	−6.6666	−1.5066	−0.8619	1.4331	3.6596	0.0097
$L_f^E(10^{-11}\mathrm{m})$	−2.4118	−0.4796	−0.3108	0.5878	1.5992	0.0045
$V^E\ (10^{-6}\,\mathrm{m^3\,mol^{-1}})$	−13.1756	−2.7015	−1.6867	2.7612	7.1065	0.0180
$\Delta\eta\ (10^{-3}\,\mathrm{N\,s\,m^{-2}})$	−0.9745	−0.1722	−0.0438	0.1432	0.1212	0.0011
$G^{*E}\ (\mathrm{kJ\,mol^{-1}})$	−1.6086	−0.3899	−0.0157	0.3251	0.3534	0.0023

Figure 1. Variation of deviations in isentropic compressibility Δk_s with mole fraction x_1 of DMSO for the binary mixtures at 30°C. Points show experimental values and curves show calculated values using equation (9).

cyclohexanol–cyclohexanol interaction; whereas the negative Δk_s and L_f^E values for DMSO + cyclohexanone/cyclohexylamine mixtures suggest the presence of specific interactions between DMSO and cyclohexanone/cyclohexylamine molecules in these mixtures, i.e., DMSO–cyclohexanone/cyclohexylamine interaction is stronger than
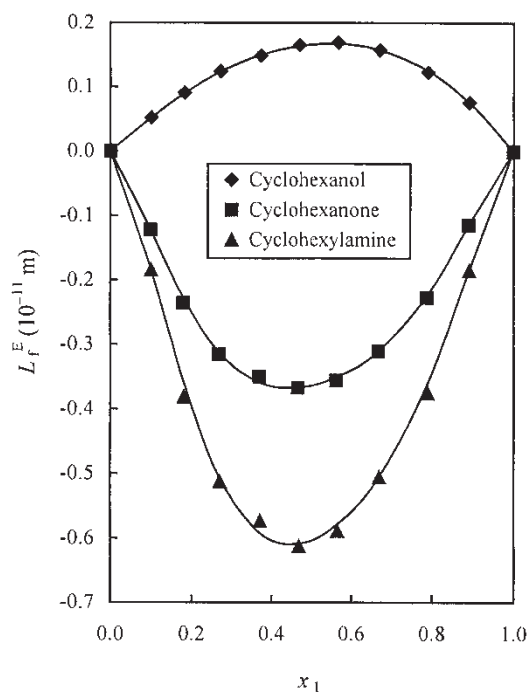
Figure 2.   Variation of excess free length L_f^E with mole fraction x_1 of DMSO for the binary mixtures at 30°C. Points show experimental values and curves show calculated values using equation (9).
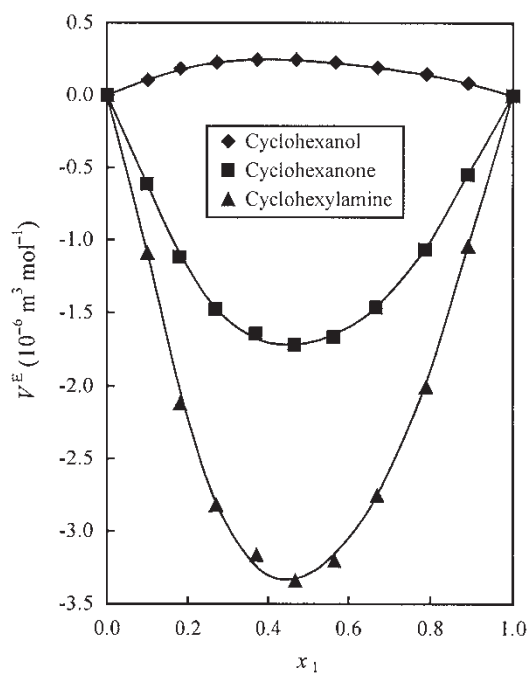
Figure 3.   Variation of excess molar volume V^E with mole fraction x_1 of DMSO for the binary mixtures at 30°C. Points show experimental values and curves show calculated values using equation (9).
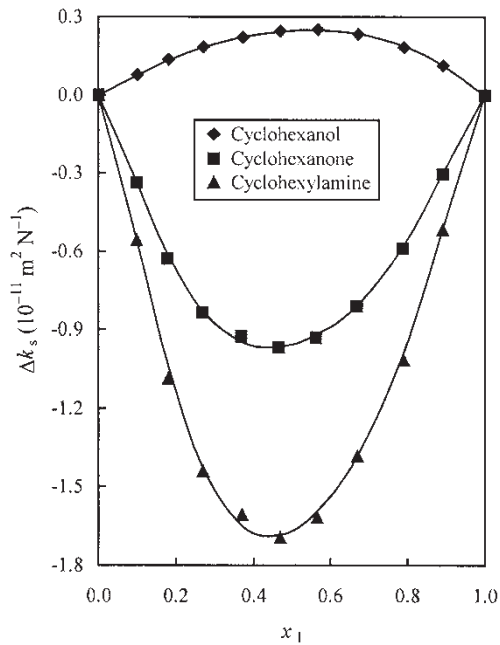
Figure 4. Variation of deviations in viscosity, $\Delta\eta$ with mole fraction x_1 of DMSO for the binary mixtures at 30°C. Points show experimental values and curves show calculated values using equation (9).

Figure 5. Variation of excess free energy of activation of viscous flow, G^{*E} with mole fraction x_1 of DMSO for the binary mixtures at 30°C. Points show experimental values and curves show calculated values using equation (9).
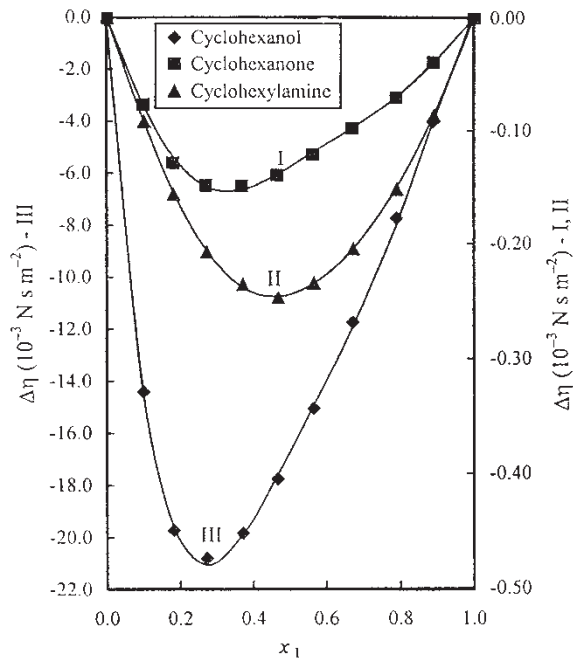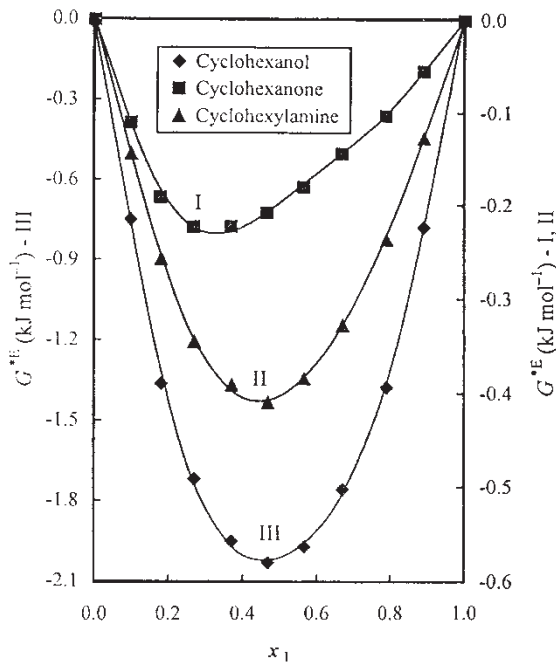
DMSO–DMSO or cyclohexanone–cyclohexanone/cyclohexylamine–cyclohexylamine interaction. The specific interactions in DMSO + cyclohexanone mixtures may be due to strong dipole–dipole interactions between unlike molecules, whereas in DMSO + cyclohexylamine mixtures may be attributed to the formation of hydrogen bond between oxygen atom of S=O group of DMSO and hydrogen atom of NH_2 group of cyclohexylamine. The magnitude of deviations in Δk_s and L_f^E values from rectilinear dependence on composition of the mixture suggest that the strength of interactions between unlike molecules would follow the order: cyclohexanol < cyclohexanone < cyclohexylamine, which is in accordance with the view proposed by Fort and Moore [18] that Δk_s becomes increasingly negative as the strength of interaction between unlike molecules in the mixture increases.

The curves in figure 3 show that, like Δk_s and L_f^E, the V^E values are small positive for DMSO + cyclochexanol mixtures and negative for DMSO + cyclohexanone/cyclohexylamine mixtures over the whole composition range. This suggests that there is an expansion in volume in case of DMSO + cyclohexanol, whereas a contraction in volume in case of DMSO + cyclohexanone/cyclohexylamine mixtures. The negative V^E values for DMSO + cyclohexanone mixtures may be attributed to strong dipole–dipole interactions, whereas for DMSO + cyclohexylamine mixtures may be due to the formation of H-bonds between DMSO and cyclohexylamine molecules. Another contribution to negative V^E values comes from the difference in the molecular sizes of DMSO and cyclohexanone/cyclohexylamine molecules in the mixtures. There is significant difference in molar volumes of DMSO ($=7.141 \times 10^{-5}\,m^3\,mol^{-1}$), cyclohexanone ($=10.469 \times 10^{-5}\,m^3\,mol^{-1}$) and cylohexylamine ($=11.535 \times 10^{-5}\,m^3\,mol^{-1}$) which may allow the geometrical fitting of smaller DMSO molecules into the voids created by bigger cyclohexanone/cyclohexylamine molecules in the mixtures [19], leading to contraction in volume, and hence, negative V^E values. The positive V^E values for DMSO + cyclohexanol mixtures suggests that the possible H-bonding S=O$\cdots$H$-$O$-$ between DMSO and cyclohexanol molecules is weaker than DMSO–DMSO and cyclohexanol–cyclohexanol interactions. Though, there is possibility of fitting of smaller DMSO molecules into the voids created by bigger cyclohexanol molecules (molar volume $= 10.637 \times 10^{-5}\,m^3\,mol^{-1}$) but this possibility seems to be dim. This may be due to the fact that cyclohexanol molecules are highly self-associated and well packed (as indicated by high viscosity, 39.5961 cP and very low value of free volume, $7.887 \times 10^{-10}\,m^3\,mol^{-1}$, calculated by using the relation [20] given by Suryanarayana) in the pure state, which might hinder the breaking up of associated cyclohexanol structures and do not allow the fitting of DMSO molecules into the well-packed structures of cyclohexanol molecules, thereby, leading to positive V^E values for DMSO + cyclohexanol mixtures. Again, the magnitude of V^E values indicates that the strength of interaction between component molecules in the mixtures under study follows the order: cyclohexanol < cyclohexanone < cyclohexylamine, which further supports the trends exhibited by Δk_s and L_f^E values.

The values of $\Delta\eta$ (figure 4) and G^{*E} (figure 5) are negative over whole composition range for all the three binary systems under study. It has been reported [21,22] that negative deviations of $\Delta\eta$ and G^{*E} occur for the mixtures having components of different molecular size, as in the case of present mixtures.

The apparent molar compressibility, $K_{\phi,2}$ and apparent molar volume, $V_{\phi,2}$ of cyclohexanol/cyclohexanone/cyclohexylamine (component 2) in DMSO were calculated by using the relations [23,24]

Table 3. The values of $\bar{K}_{\phi,2}^{\mathrm{o}}$, $K_{\phi,2}^{*}$, ΔK, $\bar{V}_{\phi,2}^{\mathrm{o}}$, $V_{\phi,2}^{*}$ and ΔV of component 2 in DMSO for the binary mixtures.

	$\bar{K}_{\phi,2}^{\mathrm{o}}$	$K_{\phi,2}^{*}$	ΔK	$\bar{V}_{\phi,2}^{\mathrm{o}}$	$V_{\phi,2}^{*}$	ΔV
Component 2	$(10^{-14}\,\mathrm{m}^5\,\mathrm{N}^{-1}\,\mathrm{mol}^{-1})$			$(10^{-6}\,\mathrm{m}^3\,\mathrm{mol}^{-1})$		
Cyclohexanol	5.277	5.426	−0.149	107.12	106.35	0.77
Cyclohexanone	4.872	5.701	−0.829	99.28	104.69	−5.41
Cyclohexylamine	5.319	6.883	−1.564	104.96	115.35	−10.40

$$K_{\phi,2} = K_{\phi,2}^{*} + K_{\mathrm{s}}^{\mathrm{E}}/x_2 \qquad (10)$$

$$V_{\phi,2} = V_2^{*} + V^{\mathrm{E}}/x_2 \qquad (11)$$

where $K_{\mathrm{s}}^{\mathrm{E}}\ [=(k_{\mathrm{s}}V)^{\mathrm{E}}]$ is the excess molar compressibility of the mixture; x_2, $K_{\phi,2}^{*}$ and V_2^{*} are the mole fraction, molar isentropic compressibility and molar volume of component 2, respectively. The partial molar compressibility, $\bar{K}_{\phi,2}^{\mathrm{o}}$ and partial molar volume, $\bar{V}_{\phi,2}^{\mathrm{o}}$ of component 2 in DMSO at infinite dilution were obtained by using the method described in the literature [23]. The deviations in $K_{\phi,2}$ and $V_{\phi,2}$ at infinite dilution, ΔK and ΔV, respectively, were calculated by using the relations [23]

$$\Delta K = \bar{K}_{\phi,2}^{\mathrm{o}} - K_{\phi,2}^{*} \qquad (12)$$

$$\Delta V = \bar{V}_{\phi,2}^{\mathrm{o}} - V_2^{*} \qquad (13)$$

The values of $\bar{K}_{\phi,2}^{\mathrm{o}}$, $K_{\phi,2}^{*}$, ΔK, $\bar{V}_{\phi,2}^{\mathrm{o}}$, V_2^{*} and ΔV are given in table 3. A close perusal of table 3 indicates that the deviations in ΔK are small negative for DMSO + cyclohexanol as compared to the remaining two mixtures which show relatively large negative deviations in ΔK. The deviations in ΔV (table 3) are small positive for DMSO + cyclohexanol and large negative for DMSO + cyclohexanone/cyclohexylamine mixtures, indicating that on mixing there is an expansion in volume for DMSO + cyclohexanol and a contraction in volume for DMSO + cyclohexanone/cyclohexylamine mixtures. The trends and magnitudes of ΔK and ΔV values (table 3) suggest that the strength of interactions in these mixtures follows the order: cyclohexanol < cyclohexanone < cyclohexylamine. This further strengthens our earlier conclusion regarding interactions in these mixtures drawn from the composition dependences of the excess functions (Δk_{s}, $L_{\mathrm{f}}^{\mathrm{E}}$, V^{E}, $\Delta\eta$ and $G^{*\mathrm{E}}$).

4. Theoretical analysis

4.1. *Isothermal compressibility*

Literature surveys indicate that very few studies [25,26] have been reported on the theoretical prediction of isothermal compressibility, k_T of liquid mixtures. Pandey *et al.* [26] predicted the k_T values of some binary liquid mixtures by using the Flory's statistical theory [27,28] and various hard sphere models [29–33] and compared the results with the experimental findings. In the present work, the values of k_T for the binary mixtures were predicted by the equation based on Flory's statistical theory and five rigid sphere equations based on various hard sphere models as given below.

Flory's statistical theory [27,28]:

$$k_T = T\tilde{V}^2\alpha/P^* \tag{14}$$

Thiele–Lebowitz model [29,30]:

$$k_T = \frac{V}{RT} \cdot \frac{(1-y)^4}{(1+2y)^2} \tag{15}$$

Thiele model [29]:

$$k_T = \frac{V}{RT} \cdot \frac{(1-y)^3}{(1+5y+9y^2-3y^3)} \tag{16}$$

Guggenhiem model [31]:

$$k_T = \frac{V}{RT} \cdot \frac{(1-y)^5}{(1+3y)} \tag{17}$$

Carnahan–Starling model [32]:

$$k_T = \frac{V}{RT} \cdot \frac{(1-y)^4}{(1+4y+4y^2-4y^3+y^4)} \tag{18}$$

Hoover–Ree model [33]:

$$k_T = \frac{V}{RT} \cdot (1+8y+30y^2+73.44y^3+141.0y^4+273.0y^5)^{-1} \tag{19}$$

where V and P^* are the reduced volume and characteristic pressure, respectively, obtained by using Flory's statistical theory; α is the coefficient of thermal expansion and y is the packing fraction. The values of α for pure liquids have been obtained from the measured density values at different temperatures and for the mixtures have been obtained by using the additive relation

$$\alpha = x_1\alpha_1 + x_2\alpha_2 \tag{20}$$

The values of y were evaluated by using the relation [26]

$$y = \pi d^3 N/6V \tag{21}$$

where N is the Avogadro's number and d is the rigid sphere diameter of the molecules of pure liquids and liquid mixtures. The values of d were calculated by using the relation [34]

$$d^{5/2} = [V/(7.21 \times 10^{19})] \cdot (\gamma^{1/4})/T_c^{1/4} \tag{22}$$

The surface tension, γ has been calculated using the relation [34]

$$\gamma = 6.3 \times 10^{-4} \rho u^{3/2} \tag{23}$$

The values of critical temperature, T_c for pure liquids were taken from the literature [35] and for the mixtures were obtained by using the similar additive equation as for α, equation (20). The theoretically predicted values of k_T, for the binary systems, by using

Table 4.   The experimental values of isothermal compressibility, k_T, theoretically calculated values of k_T by using Flory's theory and various hard sphere models and average percentage deviations, σ (%) in the calculated values for the binary mixtures.

			k_T $(10^{-10}\,\mathrm{m^2\,N^{-1}})$				
x_1	Expt.	Flory	Equation (15)	Equation (16)	Equation (17)	Equation (18)	Equation (19)
DMSO + Cyclohexanol							
0.0000	6.154	6.154	7.750	11.206	8.638	6.319	5.557
0.1009	6.074	6.089	7.646	11.018	8.515	6.248	5.536
0.1821	6.010	6.035	7.559	10.862	8.412	6.188	5.517
0.2727	5.938	5.974	7.454	10.679	8.289	6.114	5.491
0.3730	5.859	5.903	7.331	10.466	8.144	6.026	5.455
0.4703	5.783	5.832	7.205	10.251	7.997	5.936	5.416
0.5678	5.707	5.758	7.071	10.026	7.841	5.838	5.371
0.6724	5.627	5.676	6.918	9.773	7.664	5.725	5.313
0.7910	5.539	5.579	6.733	9.472	7.451	5.588	5.238
0.8922	5.468	5.492	6.566	9.203	7.259	5.462	5.165
1.0000	5.396	5.396	6.375	8.902	7.041	5.316	5.075
σ(%)=		−0.06	−30.71	−95.98	−47.65	−3.56	8.08
DMSO + Cyclohexanone							
0.0000	7.087	7.087	8.355	11.888	9.273	6.883	6.280
0.0990	6.875	6.944	8.099	11.510	8.986	6.677	6.109
0.1791	6.702	6.824	7.886	11.198	8.749	6.506	5.965
0.2687	6.523	6.686	7.672	10.881	8.508	6.334	5.825
0.3683	6.342	6.529	7.461	10.563	8.270	6.166	5.692
0.4653	6.173	6.370	7.262	10.265	8.047	6.008	5.569
0.5628	6.012	6.206	7.076	9.983	7.836	5.862	5.458
0.6679	5.849	6.022	6.890	9.699	7.626	5.716	5.350
0.7877	5.676	5.805	6.692	9.395	7.402	5.562	5.241
0.8903	5.540	5.611	6.541	9.159	7.230	5.445	5.163
1.0000	5.396	5.396	6.375	8.902	7.041	5.316	5.075
σ(%)=		−0.21	−22.57	−82.56	−38.24	2.46	11.34
DMSO + Cyclohexylamine							
0.0000	7.361	7.361	8.710	12.515	9.692	7.131	6.361
0.1000	7.087	7.195	8.401	12.044	9.343	6.888	6.175
0.1807	6.857	7.057	8.126	11.632	9.034	6.669	6.001
0.2707	6.630	6.898	7.862	11.229	8.735	6.461	5.842
0.3707	6.406	6.715	7.606	10.836	8.445	6.261	5.697
0.4679	6.200	6.531	7.365	10.465	8.172	6.073	5.560
0.5654	6.015	6.340	7.149	10.130	7.927	5.906	5.444
0.6703	5.837	6.127	6.942	9.803	7.690	5.747	5.338
0.7894	5.654	5.874	6.718	9.451	7.435	5.576	5.228
0.8913	5.526	5.647	6.558	9.191	7.250	5.455	5.159
1.0000	5.396	5.396	6.375	8.902	7.041	5.316	5.075
σ(%)=		−0.35	−22.37	−83.49	−38.26	3.09	13.43

Flory's theory and five hard sphere models were compared with the experimental k_T values calculated by using the relation

$$k_T = k_s + T\alpha^2 V/C_p \tag{24}$$

where C_p is the heat capacity. The values of C_p for pure liquids were taken from the literature [35,36] and for the mixture were obtained by using similar additive relation as for α, equation (20). The experimental k_T values, predicted values of k_T by using Flory's statistical theory and five hard sphere models and average percentage error in predicted values for all the three binary systems are given in table 4. It is clear from table 4

Table 5. Values of different parameters, calculated by using various one-, two-, and three-parameter models, along with the standard deviations, σ between theoretical and experimental η values for the binary mixture.

Model	Parameters			σ
DMSO + Cyclohexanol				
Grunberg–Nissan	$G_{12} = -3.397$			0.216
Katti–Chaudhri	$W_{vis}/RT = -3.223$			0.286
McAllister (three-body interaction)	$Z_{12} = 1.587$	$Z_{21} = 5.232$		0.207
Heric–Brewer	$\alpha_{12} = 0.208$	$\alpha_{21} = 1.966$		0.207
McAllister (four-body interaction)	$Z_{1112} = 0.402$	$Z_{1122} = 0.378$	$Z_{1222} = 0.468$	0.181
DMSO + Cyclohexanone				
Grunberg–Nissan	$G_{12} = -0.336$			0.025
Katti–Chaudhri	$W_{vis}/RT = -0.342$			0.025
McAllister (three-body interaction)	$Z_{12} = 1.521$	$Z_{21} = 1.769$		0.008
Heric–Brewer	$\alpha_{12} = -0.335$	$\alpha_{21} = 0.210$		0.008
McAllister (four-body interaction)	$Z_{1112} = 0.885$	$Z_{1122} = 0.926$	$Z_{1222} = 1.012$	0.005
DMSO + Cyclohexylamine				
Grunberg–Nissan	$G_{12} = -0.605$			0.011
Katti–Chaudhri	$W_{vis}/RT = -0.636$			0.012
McAllister (three-body interaction)	$Z_{12} = 1.325$	$Z_{21} = 1.669$		0.005
Heric–Brewer	$\alpha_{12} = -0.633$	$\alpha_{21} = 0.108$		0.005
McAllister (four-body interaction)	$Z_{1112} = 0.829$	$Z_{1122} = 0.784$	$Z_{1222} = 1.008$	0.004

that the equation (14) based on Flory's statistical theory predicts the k_T values best showing minimum percentage error. Out of the five hard sphere models tested, Carnahan–Starling equation (18) predicts the k_T values best, followed by Hoover–Ree equation (19) for the binary mixtures studied. The remaining three equations, viz. Thiele–Lebowitz equation (15), Thiele equation (16) and Guggenhiem equation (17) could not predict the k_T values well and show large deviations from the experimental k_T values.

4.2. *Viscosity*

The viscosities of all the three binary mixtures under study were correlated and predicted theoretically in terms of pure component data by using various one-parameter relations based on the models proposed by Grunberg–Nissan [37] and Katti–Chaudhri [38]; two-parameter relations based on the models proposed by McAllister (three-body interaction) [39] and Heric–Brewer [40]; and three-parameter relation based on McAllister four-body interaction model [39,41]. The values of the parameters of above mentioned correlating equations, G_{12}, $W_{vis/RT}$, Z_{12}, Z_{21}, α_{12}, α_{21}, Z_{1112}, Z_{1122} and Z_{1222} along with the standard deviations, σ are given in table 5. A close perusal of table 5 indicates that all the five equations used predict the η values best for DMSO + cyclohexylamine mixtures showing minimum standard deviation σ, followed by DMSO + cyclohexanone mixtures and then by DMSO + cyclohexanol mixtures which show maximum σ values. The values of σ for all the three systems indicate that for each system three-parameter relation predicts the data best followed by two-parameter relations and then by one-parameter relations. Therefore, it may be concluded that the predicting ability of these correlating equations increases as the number of adjustable parameters in the relation increase.

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