

# Thermodynamic Investigation of Dimethyl Sulfoxide Binary Mixtures at 293.15 and 313.15 K

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**Abstract** Densities ( $\rho$ ), speeds of sound ( $u$ ), and isentropic compressibilities ( $k_S$ ) of binary mixtures of dimethyl sulfoxide (DMSO) with water, methanol, ethanol, 1-propanol, 2-propanol, acetone and cyclohexanone have been measured over the entire composition range at 293.15 and 313.15 K. The excess molar volumes ( $V^E$ ), the deviations in speed of sound ( $u^E$ ) and the deviations in isentropic compressibility ( $k_S^E$ ) have been determined. The  $V^E$ ,  $u^E$  and  $k_S^E$  values were fitted by the Redlich-Kister polynomial equation and the  $A_k$  coefficients as well as the standard deviations ( $d$ ) between the calculated and experimental values have been derived. The results obtained are discussed from the viewpoint of the existence of interactions between the components of the binary mixtures.

**Keywords** Dimethyl sulfoxide · Density · Speed of sound · Isentropic compressibility · Excess thermodynamic properties · Molecular interactions

## 1. Introduction

Studies of the thermodynamic and ultrasonic properties of binary mixtures are of considerable importance in the fundamental understanding of the nature of the interactions between unlike molecules. In recent years there has been considerable interest in theoretical and experimental investigations of the excess thermodynamic properties of binary mixtures [1–3]. In principle, interactions between the molecules can be established from the study of the deviations from ideal behavior of physical properties such as molar volume and isentropic compressibility. The negative or positive deviations from the ideal value depend on the type

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and the extent of the interactions between the unlike molecules, as well as on the composition and the temperature. In the case of excess molar volume, when the interactions between the molecules of the mixed components are weaker than in the pure component, the excess molar volume will be positive, whereas when the association between the mixed components (the “packing effect”) predominates, the excess molar volume will be negative. The variation of the isentropic compressibility is analogous of that of the excess molar volume, whereas the change of the deviation in speed of sound tends to become the inverse.

As a continuation of our research program of determining the thermodynamic properties of binary mixtures [4–9], we report here experimental values of density ( $\rho$ ), speed of sound ( $u$ ), and isentropic compressibility ( $k_S$ ) for the binary mixtures of dimethyl sulfoxide (DMSO) with water, methanol, ethanol, 1-propanol, 2-propanol, acetone and cyclohexanone at 283.15 and 313.15 K. The excess molar volumes ( $V^E$ ), the deviations in speed of sound ( $u^E$ ), and the deviations in isentropic compressibility ( $k_S^E$ ) have been calculated. The  $V^E$ ,  $u^E$  and  $k_S^E$  values were correlated using the Redlich-Kister polynomial equation and the  $A_k$  coefficients, as well as the standard deviation ( $d$ ) between the experimental and calculated values, have been calculated. The purpose of this work is to gain some understanding about the type and magnitude of the molecular interactions in the binary mixtures of DMSO and their effect on the excess thermodynamic properties.

DMSO was particularly chosen because of its wide range of applicability as a solvent in synthetic chemistry (carbohydrates, dyes, resins, polymers), in biological processes and in pharmacy and medicine (dermatology, immunology, microbiology) [10]. DMSO exhibits dipole-dipole interactions in the pure state because of its fairly high dipole moment ( $\mu = 4.30$  D) and dielectric constant ( $\epsilon = 48.9$  at 293.15 K) [11, 12]. However, the association between DMSO molecules is weaker and does not compete with the high degree of association between alcohol molecules, which are strongly associated in the pure state through hydrogen bonding to form aggregates [13, 14]. Alcohols represent an important class of hydrogen-bonded solvents, for which the degree of association is very sensitive to temperature as well as to the carbon chain length [15]. The thermodynamic properties of binary systems of DMSO with alcohols and ketones depend on the interactions between the sulfoxide group (S=O) of DMSO and the hydroxyl (—OH) or carbonyl (C=O) group of alcohol or ketone, respectively. Such a database, which concerns thermodynamic properties of binary mixtures of DMSO with alcohols and ketones, will have great relevance in the engineering process as well as in other industrial sectors.

A survey of the literature shows that experimental data for binary mixtures of DMSO with substituted benzenes [16], water [17, 18], chlorobenzene, pyridine and methyl ethyl ketone [19], thiophene [20], alkanenitriles [21], acetonitrile [22], 2-ethoxyethanol [23], ethenylbenzene [24], anisole [25], alcohols, and glycols and polyglycols [26–29] have been already reported. The excess volumes of the binary mixtures of DMSO with water, methanol, 1-propanol and 2-propanol at 298.15 and 303.15 K have been previously reported [18, 26]. However, there are no reports on excess volumes or deviations in isentropic compressibility for the binary mixtures of DMSO which have been investigated in the present work at 293.15 and 313.15 K.

## 2. Experimental section

### 2.1. Materials

Dimethyl sulfoxide (Riedel-de Haen, 99.9%), methanol (Merck, 99.8%), ethanol (Merck, 99.8%), 1-propanol (Merck, 99.8%), 2-propanol (Merck, 99.8%), acetone (Merck, 99.8%)

**Table 1** Comparison of experimental densities ( $\rho$ ), refractive indices ( $n_D$ ), and speeds of sound ( $u$ ) of pure components with the literature values at  $T = 293.15$  K

Component	$\rho/\text{g}\cdot\text{cm}^{-3}$		$n_D$		$u/\text{m}\cdot\text{s}^{-1}$	
	exp.	lit.	exp.	Lit.	exp.	lit.
Water	0.99822	0.99821 <sup>a</sup>	1.3330	1.3328 <sup>a</sup>	1483.1	1483.0 <sup>b</sup>
Methanol	0.79144	0.79131 <sup>b</sup>	1.3290	1.3288 <sup>a</sup>	1118.4	1124.8 <sup>b</sup>
Ethanol	0.78957	0.78937 <sup>b</sup>	1.3615	1.3610 <sup>a</sup>	1159.6	1164.9 <sup>b</sup>
1-Propanol	0.80377	0.80375 <sup>b</sup>	1.3850	1.3854 <sup>a</sup>	1222.5	1225.0 <sup>b</sup>
2-Propanol	0.78525	0.78518 <sup>e</sup>	1.3780	1.3782 <sup>i</sup>	1155.8	1164.0 <sup>i</sup>
Acetone	0.79032	0.79117 <sup>c</sup>	1.3584	1.3587 <sup>c</sup>	1162.0	1163.0 <sup>k</sup>
Cyclohexanone	0.94644	0.94780 <sup>a</sup>	1.4503	1.4500 <sup>g</sup>	1413.0	1412.0 <sup>j</sup>
Dimethyl sulfoxide	1.10035	1.10050 <sup>d</sup>	1.4795	1.4789 <sup>f</sup>	1502.6	1506.7 <sup>f</sup>

<sup>a</sup>Ref. [9], <sup>b</sup>Ref. [10], <sup>c</sup>Ref. [11], <sup>d</sup>Ref. [12], <sup>e–g</sup>Values from interpolation, Refs. [13–15],

<sup>h</sup>Ref. [16], <sup>i</sup>Ref. [17], <sup>j,k</sup>Values at  $T = 298.15$  K, Refs. [18, 19].

and cyclohexanone (Riedel-de Haen, 99.8%) were used without purification. The water content as indicated by chromatographic analysis was less than 0.05%. The solvents were stored over molecular sieves (0.4 nm). The water used was doubly distilled and its specific conductivity was found to be  $0.70 \mu\text{S}$  at 293.15 K. The purity of the pure components was assessed by comparing the experimental values of density, refractive index and speed of sound with literature values at 293.15 K (Table 1). The agreement was satisfactory. The binary mixtures were prepared by mass (Mettler balance of accuracy  $\pm 0.01$  mg) and the mole fractions were known to  $\pm 0.0001$ . All molar quantities are based on the relative atomic mass table of 1985 issued by IUPAC.

## 2.2. Apparatus and procedures

Densities of pure liquids and binary mixtures were measured with a digital densimeter (Anton Paar, model DMA 58, Austria) with a built-in solid-state thermostat. The DMA cell was calibrated with dry air and doubly distilled water, whose densities at 293.15 and 313.15 K were taken from the literature [30]. The sample size was  $0.7 \text{ cm}^3$ . The uncertainty in temperature of the internal thermostat was  $\pm 0.005$  K and that of the sample thermostat was  $\pm 0.01$  K. The uncertainty of the measured value of density was  $\pm 0.00001 \text{ g}\cdot\text{cm}^{-3}$ .

The refractive indices of pure liquids at the sodium D-line were measured with a thermostatted Abbe refractometer (model A. Krüss) with a built-in light source for the prism with an accuracy of  $\pm 0.0001$ . The thermostat temperature was constant to  $\pm 0.01$  K.

The speeds of sound were measured with a digital sound analyzer (Anton Paar, model DSA 48, Austria). The temperature was maintained constant within  $\pm 0.01$  K. The sound analyzer was calibrated with dry air and doubly distilled water at 293.15 and 313.15 K. The isentropic compressibility ( $k_S$ ) was determined from density ( $\rho$ ) and speed of sound ( $u$ ) data using the equation of Laplace,  $k_S = 1/(u^2 \cdot \rho)$  [31]. The uncertainty of the measured value of speed of sound was  $\pm 1 \text{ m}\cdot\text{s}^{-1}$  and the uncertainty of the calculated isentropic compressibility values was  $\pm 1 \text{ TPa}^{-1}$ .

## 3. Results and discussion

The experimental values of density ( $\rho$ ), speed of sound ( $u$ ) and isentropic compressibility ( $k_S$ ) of binary mixtures of DMSO with water, methanol, ethanol, 1-propanol,

2-propanol, acetone and cyclohexanone at 293.15 and 313.15 K are summarized in Table 2.

The excess molar volumes ( $V^E$ ) were calculated from the difference between the real ( $V_m$ ) and the ideal molar volume ( $V_m^{\text{id}}$ ) using the density values according to the Eq. [8, 9]:

$$V^E = V_m - V_m^{\text{id}} = V_m - \sum_{i=1}^2 V_i x_i \quad (1)$$

where  $V_i$  and  $x_i$  represent the molar volume and mole fraction of the  $i$ th component, respectively. The real molar volume ( $V_m$ ) of the binary mixtures was calculated as  $V_m = (x_1 M_1 + x_2 M_2) / \rho_m$ , where  $\rho_m$  is the density of the solution and  $M_1$ ,  $M_2$  are the molar masses of each constituent. The uncertainty of the derived excess molar volumes was  $\pm 0.001 \text{ cm}^3 \cdot \text{mol}^{-1}$ . The deviations in the speed of sound ( $u^E$ ) were calculated from the speed of sound values using the following equation [32]:

$$u^E = u_m - \sum_{i=1}^2 x_i u_i \quad (2)$$

where  $u_m$  and  $u_i$  represent the speed of sound of the binary mixture and the  $i$ th pure component, respectively. The uncertainty of the derived deviations in speed of sound was  $\pm 1 \text{ m} \cdot \text{s}^{-1}$ .

In a similar manner, the deviations in isentropic compressibility ( $k_S^E$ ) were calculated from the following equation:

$$k_S^E = k_{S(m)} - \sum_{i=1}^2 y_i k_{S(i)} \quad (3)$$

where  $k_{S(m)}$  and  $k_{S(i)}$  refer to the isentropic compressibility of the mixture and  $i$ th pure component, respectively, and  $y_i$  is the volume fraction of the  $i$ th component given as:

$$y_i = x_i V_i / \sum_{i=1}^2 x_i V_i \quad (4)$$

The uncertainty of the derived deviations in isentropic compressibility was  $\pm 4 \text{ TPa}^{-1}$ . The experimental  $V^E$ ,  $u^E$  and  $k_S^E$  values of the binary mixtures are reported in Table 3.

Each set of the calculated values  $\Delta Y$  ( $V^E$ ,  $u^E$  and  $k_S^E$ ) was fitted to the Redlich-Kister [8] polynomial equation to derive the binary coefficients  $A_k$ :

$$\Delta Y = x_1 x_2 \sum_{k=0}^n A_k (2x_1 - 1)^k \quad (5)$$

In each case, the optimum number  $m$  of the  $A_k$  coefficients ( $m = n + 1$ ), was determined through an examination of the variation of standard deviation ( $d$ ) according to the equation:

$$d = \left[ \sum (\Delta Y_{\text{Calc}} - \Delta Y_{\text{Exp}})^2 / (p - m) \right]^{1/2} \quad (6)$$

**Table 2** Experimental densities ( $\rho$ ), speeds of sound ( $u$ ) and isentropic compressibilities ( $k_S$ ) of binary mixtures of DMSO at  $T = 293.15$  and  $313.15$  K

$x_1$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$u/\text{m}\cdot\text{s}^{-1}$	$k_S/\text{TPa}^{-1}$	$x_1$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$u/\text{m}\cdot\text{s}^{-1}$	$k_S/\text{TPa}^{-1}$
$T = 293.15$ K				$T = 313.15$ K			
<b>DMSO (1)+Water (2)</b>							
1.0000	1.10035	1502.6	402	1.0000	1.08022	1434.0	450
0.8406	1.10179	1534.4	386	0.8706	1.08167	1460.7	433
0.7492	1.10266	1556.9	374	0.7954	1.08272	1478.2	423
0.6076	1.10358	1599.9	354	0.6739	1.08416	1512.8	403
0.4793	1.10262	1647.5	334	0.6168	1.08465	1531.7	393
0.3769	1.09866	1687.7	320	0.5016	1.08465	1575.0	372
0.2866	1.09058	1716.0	312	0.3896	1.08190	1621.1	352
0.2561	1.08618	1721.0	311	0.2952	1.07509	1656.0	339
0.1896	1.07291	1715.6	317	0.1983	1.06043	1670.8	338
0.1326	1.05627	1684.5	334	0.0990	1.03353	1636.0	362
0.0906	1.04118	1642.7	356	0.0000	0.99225	1529.2	431
0.0541	1.02328	1582.4	390				
0.0000	0.99822	1483.1	455				
<b>DMSO (1) + Methanol (2)</b>							
1.0000	1.10035	1502.6	403	1.0000	1.08022	1434.0	450
0.9097	1.08433	1484.9	418	0.8821	1.06111	1413.5	472
0.8190	1.06962	1468.4	434	0.7905	1.04459	1394.9	492
0.7393	1.05810	1455.8	446	0.6785	1.02184	1368.7	522
0.6589	1.03666	1431.2	471	0.5919	1.00074	1344.1	553
0.6179	1.02758	1421.3	482	0.5024	0.97920	1318.5	587
0.5138	0.99899	1386.9	520	0.3916	0.94667	1278.6	646
0.4037	0.96913	1350.1	566	0.2975	0.91458	1237.9	713
0.3236	0.94117	1314.8	615	0.1977	0.87478	1186.2	812
0.2251	0.90487	1267.5	688	0.0978	0.82762	1124.5	956
0.1590	0.87613	1229.8	755	0.0000	0.77248	1052.8	1168
0.0689	0.83149	1170.6	878				
0.0000	0.79144	1118.4	1010				
<b>DMSO (1) + Ethanol (2)</b>							
1.0000	1.10035	1502.6	403	1.0000	1.08022	1434.0	450
0.8971	1.07471	1473.6	429	0.8901	1.05298	1403.6	482
0.8010	1.04976	1445.6	456	0.7961	1.02859	1376.2	513
0.6991	1.02190	1414.5	489	0.6968	1.00168	1345.7	551
0.6006	0.9936	1382.8	526	0.5995	0.97399	1314.5	594
0.5014	0.96402	1349.9	569	0.5018	0.94491	1281.9	644
0.3995	0.93202	1314.7	621	0.3987	0.91254	1240.0	713
0.2993	0.89896	1278.7	680	0.2987	0.87976	1190.0	803
0.2023	0.86539	1242.3	749	0.2048	0.84803	1140.0	907
0.1026	0.82908	1202.8	834	0.1033	0.81150	1095.9	1026
0.0000	0.78957	1159.6	942	0.0000	0.77218	1037.9	1202
<b>DMSO (1) + 1-Propanol (2)</b>							
1.0000	1.10035	1502.6	402	1.0000	1.08022	1434.0	450
0.8962	1.06827	1470.2	433	0.8927	1.04741	1400.7	487
0.7893	1.03545	1437.6	467	0.7972	1.01845	1373.0	520
0.6959	1.00707	1410.0	499	0.6964	0.98819	1341.7	562
0.6252	0.98580	1389.2	526	0.5976	0.95883	1313.1	605
0.4985	0.94804	1353.7	576	0.4903	0.92727	1283.3	655

**Table 2** Continued

$x_1$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$u/\text{m}\cdot\text{s}^{-1}$	$k_S/\text{TPa}^{-1}$	$x_1$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$u/\text{m}\cdot\text{s}^{-1}$	$k_S/\text{TPa}^{-1}$
$T = 293.15 \text{ K}$				$T = 313.15 \text{ K}$			
0.4021	0.91969	1327.8	617	0.4021	0.90160	1259.4	699
0.3011	0.89014	1301.1	664	0.3005	0.87231	1232.4	755
0.1982	0.86042	1274.4	716	0.2029	0.84447	1206.9	813
0.0993	0.83214	1248.9	771	0.1015	0.81584	1180.5	879
0.0000	0.80377	1222.5	832	0.0000	0.78747	1153.8	954
DMSO (1) + 2-Propanol (2)							
1.0000	1.10035	1502.6	402	1.0000	1.08022	1434.0	450
0.9015	1.06676	1462.3	438	0.8512	1.03030	1373.9	514
0.7969	1.03172	1420.3	480	0.7956	1.01184	1351.8	541
0.6959	0.99817	1380.4	526	0.6768	0.97284	1305.5	603
0.6050	0.96880	1346.5	569	0.6017	0.94859	1277.3	646
0.4833	0.9295	1303.1	634	0.4973	0.91531	1239.9	711
0.3989	0.90298	1274.7	682	0.4024	0.88573	1207.6	774
0.2968	0.87172	1242.4	743	0.2985	0.85421	1174.3	849
0.1986	0.84265	1213.5	806	0.2000	0.82497	1144.1	926
0.1240	0.81591	1186.8	870	0.1000	0.79635	1114.6	1011
0.0000	0.78525	1155.8	953	0.0000	0.76784	1084.8	1107
DMSO (1) + Acetone (2)							
1.0000	1.10035	1502.6	402	1.0000	1.08022	1434.0	450
0.8925	1.06835	1467.4	435	0.8850	1.04604	1395.6	491
0.7892	1.03735	1434.1	469	0.7927	1.01838	1364.4	527
0.6941	1.00867	1403.4	503	0.7036	0.99098	1334.0	567
0.6098	0.98302	1376.6	537	0.6021	0.95987	1301.0	615
0.5027	0.95003	1342.3	584	0.5049	0.92958	1266.7	670
0.4085	0.92078	1312.6	630	0.4009	0.89693	1231.4	735
0.3043	0.88800	1279.7	688	0.1987	0.83270	1163.0	888
0.2009	0.85514	1247.6	751	0.1087	0.80300	1132.2	972
0.0980	0.82212	1215.0	824	0.0000	0.76706	1093.9	1090
0.0000	0.79032	1183.4	904				
DMSO (1) + Cyclohexanone (2)							
1.0000	1.10035	1502.6	403	1.0000	1.08022	1434.0	450
0.8952	1.07655	1485.6	421	0.8952	1.05676	1416.1	472
0.8003	1.05706	1473.4	436	0.8003	1.03757	1402.6	490
0.6979	1.03800	1462.5	450	0.6979	1.01879	1390.2	508
0.6020	1.02175	1454.2	463	0.6020	1.00281	1380.6	523
0.4997	1.00596	1447.0	475	0.4997	0.98727	1371.7	538
0.4032	0.99235	1441.5	485	0.4032	0.97382	1364.8	551
0.3026	0.97934	1437.2	494	0.3026	0.96104	1358.8	564
0.2002	0.96722	1433.5	503	0.2002	0.94904	1353.3	575
0.0985	0.95621	1430.6	511	0.0985	0.93815	1348.8	586
0.0000	0.94644	1428.2	518	0.0000	0.92844	1345.0	595

where  $p$  represents the number of measurements and  $m$  the number of coefficients used for fitting the experimental data in Eq. (5). The estimated values of  $A_k$  and  $d$  for  $V^E$ ,  $u^E$  and  $k_S^E$  are presented in Table 4. In all the cases, the best fit with Eq. (5) was found by using four adjustable fitting coefficients ( $m=4$ ,  $n=3$ ). The agreement between the measured excess quantities  $V^E$ ,  $u^E$  and  $k_S^E$  and those calculated from Redlich-Kister relation was found to be satisfactory. A comparison of our  $A_k$  coefficients for the excess volume with those of

**Table 3** Excess molar volumes ( $V^E$ ), deviations in speed of sound ( $u^E$ ), and deviations in isentropic compressibility ( $k_S^E$ ) of binary mixtures of DMSO at  $T = 293.15$  and  $313.15$  K

$x_1$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	$u^E/\text{m}\cdot\text{s}^{-1}$	$k_S^E/\text{TPa}^{-1}$	$x_1$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	$u^E/\text{m}\cdot\text{s}^{-1}$	$k_S^E/\text{TPa}^{-1}$
$T = 293.15$ K				$T = 313.15$ K			
DMSO (1) + Water (2)							
1.0000	0.0000	0	0	1.0000	0.0000	0	0
0.8406	-0.3469	35	-18	0.8706	-0.2787	14	-16
0.7492	-0.5376	59	-30	0.7954	-0.4433	25	-26
0.6076	-0.7985	105	-51	0.6739	-0.6791	48	-45
0.4793	-0.9548	155	-73	0.6168	-0.7751	61	-55
0.3769	-0.9808	197	-90	0.5016	-0.9192	94	-75
0.2866	-0.9011	227	-102	0.3896	-0.9624	129	-93
0.2561	-0.8427	233	-104	0.2952	-0.8843	155	-104
0.1896	-0.6658	229	-103	0.1983	-0.6685	161	-103
0.1326	-0.4587	199	-92	0.0990	-0.3300	116	-75
0.0906	-0.3024	158	-76	0.0000	0.0000	0	0
0.0541	-0.2124	98	-49				
0.0000	0.0000	0	0				
DMSO (1) + Methanol (2)							
1.0000	0.0000	0	0	1.0000	0.0000	0	0
0.9097	-0.1175	17	-17	0.8821	-0.1809	24	-30
0.8190	-0.2355	35	-37	0.7905	-0.3134	41	-53
0.7393	-0.3300	53	-58	0.6785	-0.4498	57	-81
0.6589	-0.3920	60	-70	0.5919	-0.4608	66	-100
0.6179	-0.4481	66	-79	0.5024	-0.6089	74	-123
0.5138	-0.5100	71	-95	0.3916	-0.6470	76	-142
0.4037	-0.5452	77	-114	0.2975	-0.6297	72	-150
0.3236	-0.4700	72	-118	0.1977	-0.5328	58	-140
0.2251	-0.4796	63	-117	0.0978	-0.3338	34	-98
0.1590	-0.4020	50	-104	0.0000	0.0000	0	0
0.0689	-0.2340	26	-63				
0.0000	0.0000	0	0				
DMSO (1) + Ethanol (2)							
1.0000	0.0000	0	0	1.0000	0.0000	0	0
0.8971	-0.0736	6	-21	0.8901	-0.0835	13	-38
0.8010	-0.1367	11	-38	0.7961	-0.1416	23	-68
0.6991	-0.1805	15	-54	0.6968	-0.1926	32	-98
0.6006	-0.2027	17	-67	0.5995	-0.2219	39	-123
0.5014	-0.2298	18	-76	0.5018	-0.2365	45	-145
0.3995	-0.2318	18	-80	0.3987	-0.2201	44	-154
0.2993	-0.2147	16	-77	0.2987	-0.1939	34	-144
0.2023	-0.1781	13	-66	0.2048	-0.1878	21	-116
0.1026	-0.1104	8	-42	0.1033	-0.1193	17	-84
0.0000	0.0000	0	0	0.0000	0.0000	0	0
DMSO (1) + 1-Propanol (2)							
1.0000	0.0000	0	0	1.0000	0.0000	0.0	0
0.8962	-0.0089	-3	-16	0.8927	-0.0084	-3.2	-20
0.7893	-0.0105	-6	-30	0.7972	-0.0109	-4.2	-37
0.6959	-0.0114	-7	-39	0.6964	-0.0125	-7.2	-47
0.6252	-0.0155	-8	-43	0.5976	-0.0129	-8.1	-55
0.4985	-0.0196	-9	-48	0.4903	-0.0116	-7.9	-59

**Table 3** Continued

$x_1$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	$u^E/\text{m}\cdot\text{s}^{-1}$	$k_S^E/\text{TPa}^{-1}$	$x_1$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	$u^E/\text{m}\cdot\text{s}^{-1}$	$k_S^E/\text{TPa}^{-1}$
0.4021	-0.0224	-7	-48	0.4021	-0.0108	-7.0	-59
0.3011	-0.0203	-6	-44	0.3005	-0.0086	-5.6	-53
0.1982	-0.0156	-4	-35	0.2029	-0.0067	-3.8	-43
0.0993	-0.0101	-1	-21	0.1015	-0.0040	-1.7	-26
0.0000	0.0000	0	0	0.0000	0.0000	0.0	0
DMSO (1) + 2-Propanol (2)							
1.0000	0.0000	0	0	1.0000	0.0000	0	0
0.9015	0.0282	-6	-22	0.8512	0.0159	-8	-40
0.7969	0.0516	-12	-41	0.7956	0.0306	-11	-52
0.6959	0.0941	-17	-53	0.6768	0.0735	-16	-71
0.6050	0.1061	-19	-61	0.6017	0.0991	-18	-78
0.4833	0.1728	-20	-64	0.4973	0.1404	-19	-83
0.3989	0.1944	-19	-62	0.4024	0.1651	-18	-81
0.2968	0.1896	-16	-55	0.2985	0.1604	-15	-72
0.1986	0.1363	-11	-44	0.2000	0.1403	-10	-58
0.1240	0.0986	-12	-19	0.1000	0.0560	-5	-35
0.0000	0.0000	0	0	0.0000	0.0000	0	0
DMSO (1) + Acetone (2)							
1.0000	0.0000	0.0	0	1.0000	0.0000	0.0	0
0.8925	-0.1563	-0.9	-23	0.8850	-0.2315	0.7	-36
0.7892	-0.2856	-1.2	-42	0.7927	-0.3917	0.9	-60
0.6941	-0.3857	-1.5	-56	0.7036	-0.4893	0.9	-79
0.6098	-0.4535	-1.4	-65	0.6021	-0.5907	2.4	-96
0.5027	-0.4957	-1.6	-72	0.5049	-0.6356	1.1	-104
0.4085	-0.5013	-1.2	-73	0.4009	-0.6436	1.2	-105
0.3043	-0.4574	-0.9	-67	0.1987	-0.5097	1.5	-79
0.2009	-0.3604	0.1	-54	0.1087	-0.3066	1.3	-51
0.0980	-0.2090	0.4	-32	0.0000	0.0000	0.0	0
0.0000	0.0000	0.0	0				
DMSO (1) + Cyclohexanone (2)							
1.0000	0.0000	0	0.0	1.0000	0.0000	0	0.0
0.8952	0.0923	-9	1.5	0.8952	0.0927	-9	0.5
0.8003	0.1596	-14	2.4	0.8003	0.1585	-14	0.9
0.6979	0.2131	-18	3.2	0.6979	0.2114	-17	1.4
0.6020	0.2465	-19	3.5	0.6020	0.2412	-18	1.6
0.4997	0.2600	-18	3.6	0.4997	0.2517	-18	1.9
0.4032	0.2533	-17	3.4	0.4032	0.2472	-16	1.8
0.3026	0.2259	-14	2.8	0.3026	0.2139	-13	1.4
0.2002	0.1748	-10	2.0	0.2002	0.1663	-9	1.2
0.0985	0.0990	-5	1.0	0.0985	0.0924	-5	0.6
0.0000	0.0000	0	0.0	0.0000	0.0000	0	0.0

Nikam *et al.* [26] for mixtures of DMSO with methanol, ethanol, 1-propanol and 2-propanol at 298.15 and 303.15 K, is shown in Table 4.

The dependence of the excess molar volume ( $V^E$ ) on the mole fraction of DMSO ( $x_1$ ) for all of the binary mixtures of DMSO at 293.15 and 313.15 K is presented graphically in Figs. 1 and 2, respectively. The largest negative  $V^E$  values have been found for the binary mixture of DMSO with water. The minimum of the curve tends to shift toward the water-rich region of the mixture ( $x_1 = 0.4$ ). For the mixtures of DMSO with acetone and methanol the



**Table 4** Parameters  $A_k$  of the Redlich-Kister equation (Eq. (5)) and standard deviations ( $d$ ) of excess functions of binary mixtures of DMSO at  $T = 293.15$  and  $313.15$  K

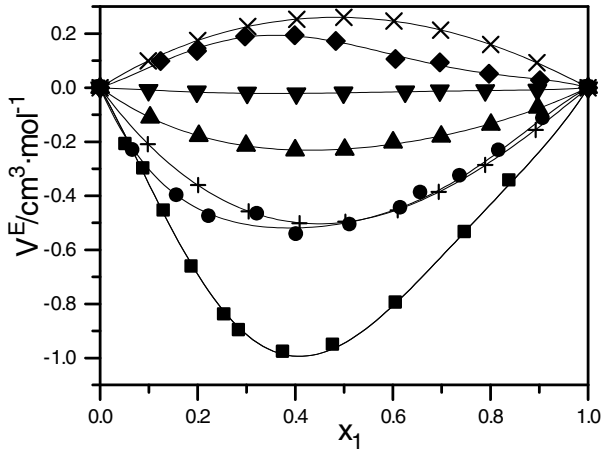
Excess function	$A_0$	$A_1$	$A_2$	$A_3$	$d$
DMSO + Water					
$T = 293.15$ K					
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-3.783	2.020	0.760	-1.861	0.016
$k_S^E/\text{TPa}^{-1}$	-417.61	-70.15	95.76	-8.97	0.755
$u^E/\text{m} \cdot \text{s}^{-1}$	587.96	-882.64	741.19	-182.97	1.420
$T = 313.15$ K					
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-3.723	1.801	0.847	-1.555	0.009
$k_S^E/\text{TPa}^{-1}$	-411.97	-137.06	40.56	55.98	0.107
$u^E/\text{m} \cdot \text{s}^{-1}$	379.53	-638.95	535.06	-172.80	1.246
DMSO + Methanol					
$T = 293.15$ K					
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-2.006	0.637	-0.556	0.945	0.022
$V^E/\text{cm}^3 \cdot \text{mol}^{-1a}$	-2.527	1.555	-0.916	-1.128	
$k_S^E/\text{TPa}^{-1}$	-466.56	148.38	-59.65	7.32	0.231
$u^E/\text{m} \cdot \text{s}^{-1}$	296.39	-80.12	24.29	-49.38	1.483
$T = 313.15$ K					
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-2.351	1.446	-0.709	-0.430	0.024
$V^E/\text{cm}^3 \cdot \text{mol}^{-1b}$	-2.730	-1.268	-0.292	-0.252	
$k_S^E/\text{TPa}^{-1}$	-580.88	203.02	-40.25	-16.13	0.669
$u^E/\text{m} \cdot \text{s}^{-1}$	295.38	-110.59	24.37	24.22	1.398
DMSO + Ethanol					
$T = 293.15$ K					
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-0.909	0.222	-0.171	0.011	0.003
$V^E/\text{cm}^3 \cdot \text{mol}^{-1a}$	-1.457	-0.051	-0.591	0.550	
$k_S^E/\text{TPa}^{-1}$	-313.96	80.49	-27.22	8.19	0.081
$u^E/\text{m} \cdot \text{s}^{-1}$	72.55	-5.84	6.16	-11.53	0.126
$T = 313.15$ K					
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-0.914	-0.026	-0.227	0.559	0.007
$V^E/\text{cm}^3 \cdot \text{mol}^{-1b}$	-1.771	0.515	0.174	0.551	
$k_S^E/\text{TPa}^{-1}$	-592.53	142.26	10.70	90.53	0.393
$u^E/\text{m} \cdot \text{s}^{-1}$	173.40	-12.48	-70.52	0.612	1.398
DMSO + 1-Propanol					
$T = 293.15$ K					
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-0.076	0.065	-0.025	-0.092	0.001
$V^E/\text{cm}^3 \cdot \text{mol}^{-1a}$	-0.885	0.040	0.106	0.278	
$k_S^E/\text{TPa}^{-1}$	-191.37	41.92	-23.15	11.91	0.103
$u^E/\text{m} \cdot \text{s}^{-1}$	-33.66	-6.36	14.61	-8.72	0.372
$T = 313.15$ K					
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-0.047	-0.021	-0.025	-0.009	0.001
$V^E/\text{cm}^3 \cdot \text{mol}^{-1b}$	-0.739	-0.118	0.342	0.049	
$k_S^E/\text{TPa}^{-1}$	-233.28	48.89	-29.03	6.69	0.490
$u^E/\text{m} \cdot \text{s}^{-1}$	-31.84	-7.96	13.77	3.73	0.349
DMSO + 2-Propanol					
$T = 293.15$ K					
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	0.657	-0.742	-0.112	0.689	0.008
$V^E/\text{cm}^3 \cdot \text{mol}^{-1a}$	0.515	-0.116	0.027	-0.182	
$k_S^E/\text{TPa}^{-1}$	-258.51	56.49	27.38	-105.71	0.353
$u^E/\text{m} \cdot \text{s}^{-1}$	-78.69	-14.30	-1.38	56.74	1.044

**Table 4** Continue.

Excess function	$A_0$	$A_1$	$A_2$	$A_3$	$d$
$T = 313.15 \text{ K}$					
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	0.566	-0.707	-0.210	0.529	0.006
$V^E/\text{cm}^3\cdot\text{mol}^{-1b}$	-0.381	4.651	5.922	-18.787	
$k_S^E/\text{TPa}^{-1}$	-328.00	46.26	-35.88	36.03	0.244
$u^E/\text{m}\cdot\text{s}^{-1}$	-76.23	-1.001	29.84	-4.090	0.116
DMSO + Acetone					
$T = 293.15 \text{ K}$					
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-1.992	0.428	0.022	0.057	0.002
$k_S^E/\text{TPa}^{-1}$	-286.47	74.02	-25.09	17.38	0.117
$u^E/\text{m}\cdot\text{s}^{-1}$	-6.042	-2.234	6.041	-10.84	0.095
$T = 313.15 \text{ K}$					
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-2.560	0.667	-0.433	-0.083	0.010
$k_S^E/\text{TPa}^{-1}$	-413.88	115.50	-45.88	32.67	0.417
$u^E/\text{m}\cdot\text{s}^{-1}$	4.200	-2.569	9.320	-2.317	0.507
DMSO + Cyclohexanone					
$T = 293.15 \text{ K}$					
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	1.040	-0.068	0.013	-0.024	0.001
$k_S^E/\text{TPa}^{-1}$	14.22	-4.30	-0.5299	2.99	0.030
$u^E/\text{m}\cdot\text{s}^{-1}$	-74.05	-22.08	-4.488	-2.251	0.251
$T = 313.15 \text{ K}$					
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	1.012	-0.027	0.004	-0.014	0.001
$k_S^E/\text{TPa}^{-1}$	6.87	-4.46	-1.04	1.61	0.053
$u^E/\text{m}\cdot\text{s}^{-1}$	-70.75	-23.53	-5.362	-4.027	0.181

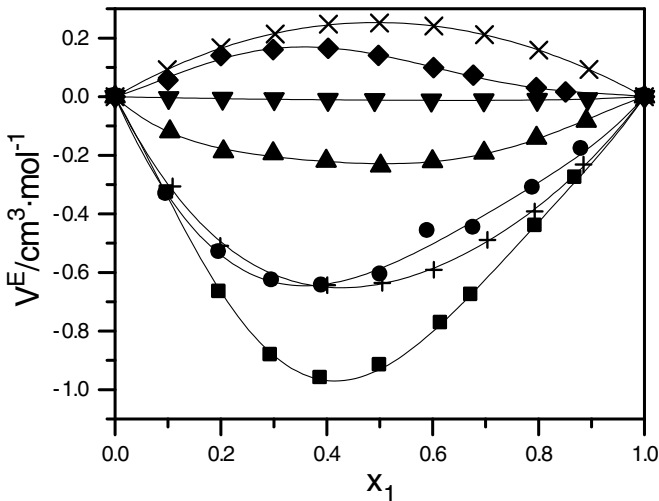
<sup>a,b</sup>Parameters of Redlich-Kister equation (Eq. 5) at  $T = 298.15$  and  $303.15 \text{ K}$ , respectively, reported by Nikam *et al.* [26]

results of  $V^E$  vary almost identically and are negative. Similarly, for the mixtures of DMSO with ethanol the  $V^E$  values are negative but less negative as compared to water-, methanol- or acetone-containing mixtures. In the case of the binary system of DMSO with 1-propanol, the  $V^E$  values are slightly negative (the binary system shows almost ideal behavior), whereas for the 2-propanol- or cyclohexanone-containing mixtures the  $V^E$  values are positive. For the equimolar mixtures ( $x_1 = x_2 = 0.5$ ) the algebraic values of  $V^E$  at both temperatures fall in the order: cyclohexanone > 2-propanol > 1-propanol > ethanol > acetone > methanol > water. The  $V^E$  values for the binary mixtures of DMSO with methanol, ethanol, 1-propanol and 2-propanol reported by Nikam *et al.* [26] at 298.15 and 303.15 K follow the same trend (2-propanol > 1-propanol > ethanol > methanol) indicating an absolute agreement with our  $V^E$  values. Furthermore, our results for the mixtures of DMSO with water are in agreement with the results reported by Aralaguppi *et al.* at 298.15 K [18]. The effect of temperature on the  $V^E$  results is almost negligible. The algebraic values of  $V^E$  decrease insignificantly with increasing temperature. The excess volumes can be considered to be affected by the following effects: the association between unlike molecules through dipole-dipole interactions (heteroassociation) and the “packing effect” [33]. The negative  $V^E$  values indicate a contraction of the volume and can be explained in terms of the heteroassociation in the mixture. Conversely, the positive values of  $V^E$  indicate that the “packing effect” of the self-associated pure components predominates over the heteroassociation with a subsequent expansion of the volume.

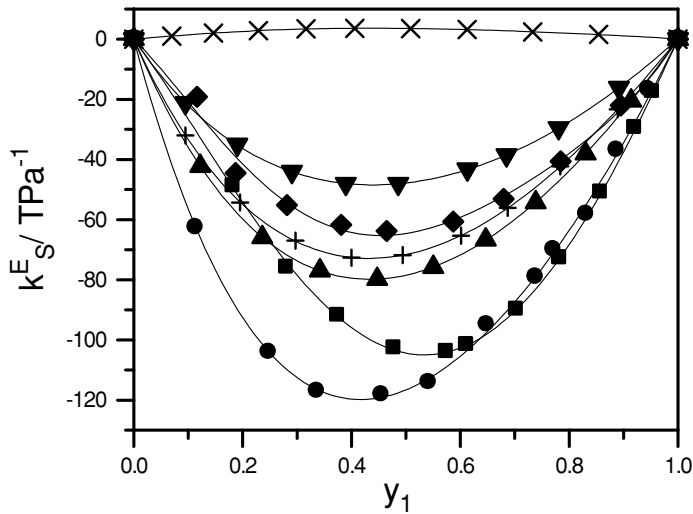


**Fig. 1** Excess molar volume ( $V^E$ ) versus the mole fraction of DMSO ( $x_1$ ) for binary mixtures of DMSO with water (■), methanol (●), ethanol (▲), 1-propanol (▼), 2-propanol (◆), acetone (+), and cyclohexanone (x) at  $T = 293.15 \text{ K}$

The large negative  $V^E$  values, which have been found for the mixtures of DMSO with water, suggest the strongest association occurs in this binary system since the  $-\text{OH}$  group of water comprises the greatest available surface area for interaction with the  $\text{S} = \text{O}$  group of DMSO, compared to  $-\text{OH}$  or  $\text{C} = \text{O}$  groups of alcohol and ketone, respectively. The progressive increase of the  $V^E$  values for the binary systems, which contain methanol, ethanol, 1-propanol and 2-propanol, respectively, follows the expected decrease of the  $-\text{OH}$  group proton donor capacity with the increase of the alcohol chain length, and suggests that the strength of the interactions involving alcohols decreases with the increase of the size of

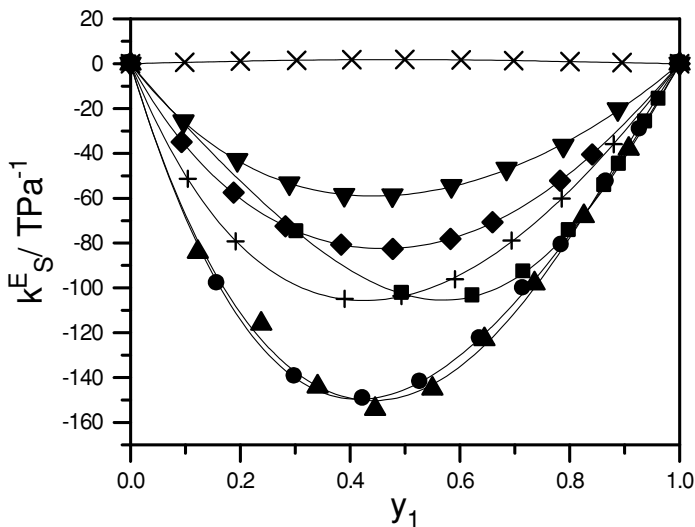


**Fig. 2** Excess molar volume ( $V^E$ ) versus the mole fraction of DMSO ( $x_1$ ) for binary mixtures of DMSO with water (■), methanol (●), ethanol (▲), 1-propanol (▼), 2-propanol (◆), acetone (+), and cyclohexanone (x) at  $T = 313.15 \text{ K}$

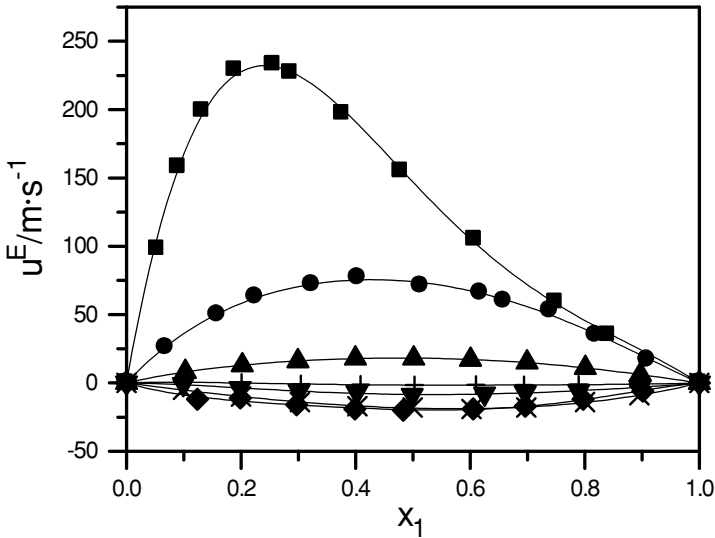


**Fig. 3** Deviation in the isentropic compressibility ( $k_S^E$ ) versus the volume fraction of DMSO ( $y_1$ ) for binary mixtures of DMSO with water (■), methanol (●), ethanol (▲), 1-propanol (▼), 2-propanol (◆), acetone (+), and cyclohexanone (x) at  $T = 293.15$  K

the alcohol [34, 35]. The difference concerning the variation of  $V^E$  that has been observed among acetone- and cyclohexanone-containing mixtures is considered to be attributed to the difference in the size between the two ketone molecules; in other words, to the effect of the “steric hindrance”. Cyclohexanone is larger than acetone and consequently the “packing



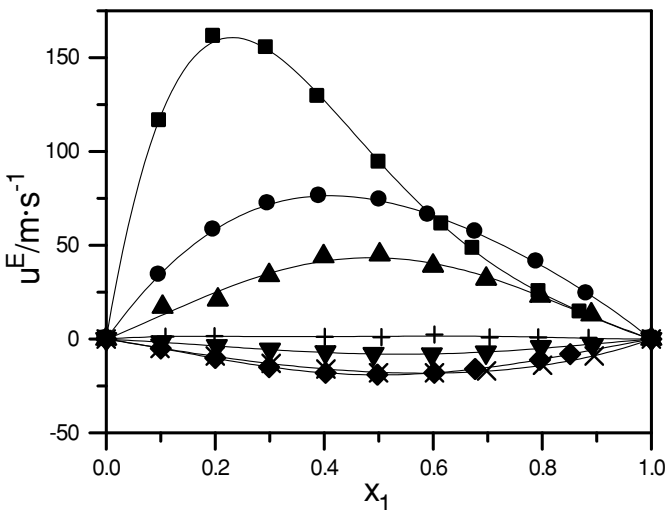
**Fig. 4** Deviation in the isentropic compressibility ( $k_S^E$ ) versus the volume fraction of DMSO ( $y_1$ ) for binary mixtures of DMSO with water (■), methanol (●), ethanol (▲), 1-propanol (▼), 2-propanol (◆), acetone (+), and cyclohexanone (x) at  $T = 313.15$  K



**Fig. 5** Deviation in speed of sound ( $u^E$ ) versus the mole fraction of DMSO ( $x_1$ ) for binary mixtures of DMSO with water (■), methanol (●), ethanol (▲), 1-propanol (▼), 2-propanol (◆), acetone (+), and cyclohexanone (x) at  $T = 293.15 \text{ K}$

effect” between like molecules is more dominant than the heteroassociation, resulting in an increase of the excess volume.

The dependence of the deviations in isentropic compressibility ( $k_S^E$ ) on the mole fraction of DMSO ( $x_1$ ) for the DMSO binary mixtures at 293.15 and 313.15 K is presented graphically in Figs. 3 and 4. Except for the cyclohexanone-containing mixtures, for all the other binary mixtures the values of  $k_S^E$  are negative suggesting the presence of specific interactions between



**Fig. 6** Deviation in speed of sound ( $u^E$ ) versus the mole fraction of DMSO ( $x_1$ ) for binary mixtures of DMSO with water (■), methanol (●), ethanol (▲), 1-propanol (▼), 2-propanol (◆), acetone (+), and cyclohexanone (x) at  $T = 313.15 \text{ K}$

the mixing components. The algebraic values of  $k_S^E$  decrease with an increase of temperature indicating an amplification of heteroassociation with the rise in temperature. A different trend has been observed in the mixtures of DMSO with cyclohexanone, suggesting that the “packing effect” of the self-associated pure components predominates over heteroassociation, as indicated also by the  $V^E$  results.

The deviations in speed of sound ( $u^E$ ) are presented graphically *versus* the mole fraction of DMSO ( $x_1$ ) in Figs. 5 and 6. The results of  $u^E$  suggest that the extent of the interactions between unlike molecules increases in the same order as indicated by the  $k_S^E$  results.

#### 4. Conclusions

In the present paper the excess volumes ( $V^E$ ), the deviations in speed of sound ( $u^E$ ) and the deviations in isentropic compressibility ( $k_S^E$ ) for the binary mixtures of DMSO with water, methanol, ethanol, 1-propanol, 2-propanol, acetone and cyclohexanone have been derived at 293.15 and 313.15 K. The values of  $V^E$ ,  $u^E$  and  $k_S^E$  were correlated to the Redlich-Kister Eq. [33] and the  $A_k$  coefficients, as well as the standard deviations ( $d$ ) between the calculated and experimental excess properties have been derived. The results indicated the existence of specific interactions between the components for all the binary mixtures of DMSO with the only exception being the cyclohexanone-containing mixtures. For this system, the “packing effect” between like molecules appears to be more significant. The heteroassociation is amplified with the rise of temperature.

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