

# Molecular interaction study in binary mixture of DMSO with formamide and N, N-dimethylformamide

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Ultrasonic, volumetric and viscometric investigations have been carried out on DMSO + formamide and DMSO + N, N-dimethylformamide mixtures at three temperatures 293, 303 and 313 K over the entire mole fraction range. From these data, deviation in isentropic compressibility ( $\Delta k_s$ ), excess Gibb's free energy of activation for viscous flow ( $\Delta G^{*E}$ ), excess internal pressure ( $\pi_i^E$ ) and excess molar enthalpy ( $H_m^E$ ) have been calculated. A Redlich-Kister polynomial equation of third degree has been used to correlate the derived properties of binary liquid mixtures by using the least square method. The observed positive and negative values of excess parameters have been used to study the nature and strength of intermolecular interactions present in these mixtures. Further, theoretical values of ultrasonic velocity have been evaluated using theories and empirical relations.

**Keywords:** Ultrasonic velocity, Isentropic compressibility, Molar enthalpy, Dimethylsulfoxide, Amides

## 1 Introduction

The ultrasonic velocity measurements have been adequately employed in understanding the nature of molecular system and physico-chemical behavior in liquid mixtures. Studies of phase equilibrium behaviour and the excess properties of liquid mixtures are of great importance for the design of separation process and theoretical understanding of the nature of molecular interactions<sup>1</sup>. Thermodynamic and transport properties of binary mixtures of formamide and N, N-dimethylformamide with different organic liquid mixtures have been studied earlier<sup>1-3</sup>. Formamide (FA) and N,N-dimethylformamide (DMF) are well known materials that are used as a selective solvents in extraction or extractive distillation process. Dimethylsulfoxide (DMSO) is important because of its utilization in a broad range of applications in medicine<sup>4</sup>. It easily penetrates biological membranes, facilitates chemical transports in the biological tissues and is well known for its cryoprotective effects on biological systems<sup>5-7</sup>. Also well established use of DMSO as an anti-inflammatory agent is important for arthritic conditions<sup>7</sup>. Unique properties of DMSO have been exploited for several decades and its application in many areas of science<sup>8</sup>.

DMSO is aprotic, strongly associative due to highly polar S = O group in the molecules<sup>9</sup> and has large dipole moment and dielectric constants<sup>10</sup>. Formamides are polar (hydrophilic) aprotic solvent with a high dipole moment and dielectric constant. The thermodynamic properties of binary mixtures containing polar and associated components exhibit significant deviation from ideality, arising not only from the difference in size and shape but also from possible hydrogen bonding interaction between unlike molecules.

The applications of these solvents and their mixtures in chemical industry and modern technology and close relationship of formamide (FA) and N, N-dimethyl formamide (DMF) to peptides and proteins motivated us to undertake the present investigation. With this in view, we report here ultrasonic velocity, density and viscosity of binary mixtures of DMSO with formamide and N, N-dimethylformamide at varying temperatures over the entire range of composition. From these experimental data, deviation in isentropic compressibility ( $\Delta k_s$ ), excess free energy of activation of viscous flow ( $\Delta G^{*E}$ ), excess internal pressure ( $\pi_i^E$ ) and excess molar enthalpy ( $H_m^E$ ) were calculated. These parameters are temperature sensitive and provide significant information regarding inter

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molecular interactions between the component molecules. Further, the ultrasonic velocity for both the mixtures were theoretically evaluated by collision factor theory (CFT), Nomoto, Junjie and Van Dael and Vangeel's ideal mixing relations. The results have been discussed in terms of average percentage deviation (APD).

## 2 Experimental Details

Experimental liquids, DMSO, formamide and N, N dimethylformamide obtained from, Ranbaxy Fine Chemicals Limited, were purified by standard procedure, discussed by Perrin and Armarego<sup>11</sup>. All the mixtures were prepared by weight in dry and special air tight bottles. The weighing were done on a Sartorius (BP 121S) electronic single pan balance with a precision of  $\pm 0.1$  mg. The probable error in the mole fraction was estimated to be less than  $\pm 0.0001$ .

The ultrasonic velocity was measured using the ultrasonic interferometer (model M83) supplied by Mittal Enterprises, New Delhi. The instrument was calibrated by measuring the velocity in standard liquids, e.g., AR grade benzene and carbon tetrachloride. Our measured values of ultrasonic velocity ( $u$ ) for benzene and carbon tetrachloride agree closely with the literature value<sup>12</sup>. Maximum possible experimental error in ultrasonic velocity has been found to be  $\pm 0.08\%$ . The temperature of the test liquid and the binary mixtures was controlled by circulating water around the liquid cell from thermostatically controlled adequately stirred water bath (accuracy  $\pm 0.1$  °C). The density and viscosity of liquids and liquid mixtures have been measured using a single capillary calibrated pycnometer and Ostwald's viscometer as described earlier<sup>13</sup> with an accuracy of  $\pm 0.5\%$ .

## 3 Theory

From the experimental data of density, ultrasonic velocity and viscosity, various acoustical parameters such as isentropic compressibility ( $k_s$ ), Gibb's free energy of activation of viscous flow ( $\Delta G^*$ ) and internal pressure ( $\pi_i$ ) have been evaluated by standard equations<sup>14-16</sup>. The deviation /excess parameters were calculated using following equations:

Deviation in isentropic compressibility ( $\Delta k_s$ ):

$$\Delta k_s = \frac{1}{u^2 \rho} - \left( \frac{x_1}{u_1^2 \rho_1} + \frac{x_2}{u_2^2 \rho_2} \right) \quad \dots (1)$$

Excess Gibb's free energy of activation:

$$\Delta G^{*E} = RT \left[ \ln \left( \frac{\eta V}{N_A h} \right) - x_i \ln \left( \frac{\eta_i V_i}{N_A h} \right) \right] \quad \dots (2)$$

Excess internal pressure:

$$\pi_i^E = bRT(k)^{1/2} \left[ \frac{\eta^{1/2} \rho^{2/3}}{u^{1/2} M^{7/6}} - \left( \frac{x_i \eta_i^{1/2} \rho_i^{2/3}}{u_i^{1/2} M_i^{7/6}} \right) \right] \quad \dots (3)$$

Excess molar enthalpy:

$$H_m^E = x_1 \pi_{i1} V_1 + x_2 \pi_{i2} V_2 - \pi_{im} V \quad \dots (4)$$

In Eqs (1) to (4)  $u$ ,  $\rho$ ,  $\eta$ ,  $R$ ,  $T$ ,  $V$ ,  $N_A$ ,  $h$  and  $M$  stand for ultrasonic velocity, density, viscosity, universal gas constant, temperature, molar volume, Avagadro number, Planck constant and molecular weight of mixtures, respectively.  $x_i$ ,  $u_i$ ,  $\rho_i$ ,  $\eta_i$ ,  $V_i$ , ( $i=1, 2$ ) denote the mole fraction, ultrasonic velocity, density, viscosity and molar volume of  $i^{\text{th}}$  component, respectively. Here  $b$  is the packing factor,  $k$  is dimensionless constant having value of  $4.28 \times 10^9$  and independent of temperature and nature of liquid.

The deviation/excess parameters ( $\Delta k_s$ ,  $\Delta G^{*E}$ ,  $\pi_i^E$  and  $H_m^E$ ) were fitted to Redlich-Kister equation<sup>17</sup>:

$$Y^E = x_1 x_2 \sum_{i=1}^3 a_i (x_1 - x_2)^i \quad \dots (5)$$

Coefficients  $a_i$  were obtained by fitting equation to experimental results using least squares regressions method. In such case, the optimum number of coefficient is ascertained from an examination of the variation of standard deviation:

$$\sigma(Y^E) = \left[ \frac{\sum (x_{\text{expt}} - x_{\text{cal}})^2}{(N - n)} \right]^{1/2} \quad \dots (6)$$

where  $N$  is the number of data points and  $n$  is number of coefficients.

Further, various empirical/semi empirical

relations and theory for the prediction of ultrasonic velocity of liquid mixtures were used as described earlier<sup>24</sup>.

#### 4 Results and Discussion

Tables 1 and 2 represent the experimental ultrasonic velocity ( $u$ ), density ( $\rho$ ) and viscosity ( $\eta$ ) along with excess parameters over the entire mole fraction range for binary mixtures of DMSO with formamide and N, N-dimethylformamide at temperatures 293, 303 and 313 K. The values of coefficient  $a_i$ 's obtained from Eq. (5) along with standard deviation are given in Table 3. The

parameters  $\Delta k_s$ ,  $\Delta G^{*E}$ ,  $\pi_i^E$  and  $H_m^E$  plotted against the mole fraction of DMSO ( $x_1$ ) are given in Figs 1-4.

The values of excess parameters for the binary mixtures of DMSO with FA and DMF may be explained as a result of cumulative manifestation of various types of intermolecular interactions between components. Earlier workers<sup>18</sup> have reported that three main types of contributions to the excess thermodynamic properties of mixtures are:

(i) Physical: Due to non-specific Vander Waal's

Table 1 — Experimental ultrasonic velocity ( $u$ ), density ( $\rho$ ), viscosity ( $\eta$ ), deviation in isentropic compressibility ( $\Delta k_s$ ), excess gibb's free energy of activation ( $\Delta G^{*E}$ ), excess internal pressure ( $\pi_i^E$ ) and excess molar enthalpy for DMSO+formamide mixture with mole fraction  $x_1$  at three temperatures

$x_1$	$\rho$ (kg/m <sup>3</sup> )	$u$ (m/sec)	$\eta$ (mPa·s)	$\Delta k_s$ (Pa <sup>-1</sup> )	$\Delta G^{*E}$ (joule/mol)	$\pi_i^E$ (atm)	$H_m^E$ (joule/mol)
$T=293$ K							
0.0000	1137.598	1608.0	3.6509	0.0000	0.0000	0.0000	0.0000
0.0604	1133.659	1603.1	3.5674	-0.0082	197.06	5.08	-2279.6582
0.1261	1130.669	1592.3	3.4366	-0.0192	383.00	8.48	-4406.0099
0.1982	1127.974	1583.4	3.2774	-0.0431	554.79	9.90	-6281.2848
0.2776	1126.147	1571.6	3.1021	-0.0846	707.51	9.20	-7807.7368
0.3654	1123.350	1562.0	2.9161	-0.1039	833.55	11.55	-9112.0506
0.4543	1118.686	1552.9	2.7288	-0.1270	921.42	13.91	-9898.3445
0.5739	1114.440	1543.6	2.5417	-0.1164	948.70	19.18	-10098.933
0.6979	1114.856	1535.4	2.3569	-0.0901	878.56	23.40	-9195.7215
0.8391	1109.481	1526.7	2.1763	-0.0441	630.57	21.82	-6405.3980
1.0000	1103.094	1518.9	2.0001	0.0000	0.0000	0.000	0.0000
$T=303$ K							
0.0000	1129.301	1588.7	2.7146	0.0000	0.0000	0.0000	0.0000
0.0604	1125.978	1582.7	2.6884	-0.0177	212.08	7.50	-2155.1007
0.1261	1122.329	1570.9	2.6140	-0.0418	410.91	12.49	-4138.6676
0.1982	1112.506	1561.2	2.5092	-0.0706	593.58	16.02	-5922.9571
0.2776	1116.808	1550.0	2.3858	-0.1161	754.93	17.08	-7379.9987
0.3654	1110.537	1538.5	2.2495	-0.1394	887.04	20.04	-8610.3580
0.4543	1109.918	1528.0	2.1088	-0.1625	977.94	22.55	-9363.2019
0.5739	1105.770	1516.9	1.9656	-0.1594	1004.25	26.00	-9507.8046
0.6979	1104.157	1504.4	1.8224	-0.1328	927.48	27.97	-8631.3097
0.8391	1099.661	1492.8	1.6811	-0.0792	663.95	23.61	-5986.5658
1.0000	1093.171	1478.0	1.5420	0.0000	0.0000	0.0000	0.0000
$T=313$ K							
0.0000	1121.125	1567.6	2.113	0.00	0.0000	0.000	0.0000
0.0604	1117.319	1563.0	2.1208	-0.0436	238.24	13.00	-2129.3593
0.1261	1113.571	1557.9	2.0833	-0.0847	457.40	22.98	-4098.7115
0.1982	1115.813	1552.3	2.0164	-0.1259	654.96	30.47	-5865.7769
0.2776	1109.545	1544.9	1.9307	-0.1594	825.77	36.27	-7398.7064
0.3654	1105.507	1537.0	1.8321	-0.1917	961.77	39.98	-8576.5328
0.4543	1101.213	1529.3	1.7274	-0.2240	1050.62	41.44	-9258.5178
0.5739	1097.013	1513.9	1.6192	-0.2251	1068.49	42.14	-9329.8482
0.6979	1098.330	1495.1	1.5096	-0.1939	976.31	39.82	-8408.1664
0.8391	1091.197	1469.1	1.4003	-0.1361	690.14	29.06	-5740.9040
1.0000	1082.711	1434.0	1.2920	0.0000	0.0000	0.0000	0.0000

Table 2 — Experimental ultrasonic velocity ( $u$ ), density ( $\rho$ ), viscosity ( $\eta$ ), deviation in isentropic compressibility ( $\Delta k_s$ ), excess Gibb's free energy ( $\Delta G^{*E}$ ), excess internal pressure ( $\pi_i^E$ ) and excess molar enthalpy ( $H_m^E$ ) for DMSO+N,N dimethyl formamide mixtures with mole fraction  $x_1$  at three temperatures

$x_1$	$\rho$ (kg/m <sup>3</sup> )	$u$ (m/sec)	$\eta$ (mPa·s)	$\Delta k_s$ (Pa <sup>-1</sup> )	$\Delta G^{*E}$ (joule/mol)	$\pi_i^E$ (atm)	$H_m^E$ (joule/mol)
$T = 293 \text{ K}$							
0.0000	953.155	1492.0	0.82530	0.0000	0.00	0.00	0.0000
0.0940	966.372	1489.5	0.90633	0.0244	7.27	-3.54	137.1687
0.1895	979.456	1488.9	0.99486	0.0383	16.81	-6.15	225.3825
0.2862	999.843	1487.6	1.09097	0.0572	26.60	-7.48	242.1801
0.3845	1007.867	1487.7	1.19521	0.0691	35.05	-7.97	224.8030
0.4832	2021.845	1490.3	1.30675	0.0665	40.79	-8.02	203.6940
0.5838	1060.058	1493.8	1.42717	0.0614	42.86	-7.34	160.9003
0.6862	1054.236	1498.5	1.55710	0.0507	40.37	-6.15	113.8227
0.7889	1071.212	1503.5	1.69451	0.0410	32.77	-4.31	53.96301
0.8943	1089.021	1510.7	1.84324	0.0219	19.31	-2.29	18.8082
1.0000	1103.094	1519.0	2.00010	0.0000	0.00	0.00	0.0000
$T = 303 \text{ K}$							
0.0000	943.324	1448.0	0.69940	0.0000	0.0000	0.0000	0.0000
0.0940	957.018	1447.0	0.76658	0.0192	4.65	-2.76	101.2400
0.1895	969.826	1446.1	0.83734	0.0386	11.21	-4.59	150.7711
0.2862	983.223	1445.8	0.91167	0.0548	18.27	-5.65	162.7479
0.3845	998.372	1447.7	0.98988	0.0572	24.61	-6.29	166.1945
0.4832	1012.066	1450.7	1.07126	0.0549	29.15	-6.38	152.2265
0.5838	1050.005	1454.7	1.15692	0.0474	31.09	-5.99	129.2179
0.6862	1043.835	1460.7	1.24716	0.0304	29.67	-5.35	114.9314
0.7889	1061.081	1466.7	1.34053	0.0162	24.35	-4.16	88.6293
0.8943	1078.113	1472.6	1.43955	0.0056	14.52	-2.38	50.2429
1.0000	1093.171	1478.0	1.54000	0.0000	0.0000	0.00	0.0000
$T = 313 \text{ K}$							
0.0000	934.343	1411.0	0.6205	0.00	0.0000	0.000	0.0000
0.0940	947.010	1412.0	0.6689	0.0019	16.81	-1.58	20.9175
0.1895	960.720	1413.1	0.7212	0.0042	30.82	-2.68	27.0474
0.2862	974.286	1414.0	0.7774	0.0076	41.70	-3.37	20.3219
0.3845	988.449	1415.2	0.8378	0.0121	49.00	-3.66	3.7157
0.4832	1001.729	1417.1	0.9019	0.0151	52.30	-3.64	-14.6211
0.5838	1040.413	1420.3	0.9706	0.0108	51.35	-3.49	-19.6620
0.6862	1034.355	1423.2	1.0441	0.0055	45.82	-3.08	-19.9858
0.7889	1051.093	1427.0	1.1215	0.0020	35.64	-2.37	-18.3431
0.8943	1067.883	1430.2	1.2047	0.0003	20.38	-1.35	-12.8975
1.0000	1082.711	1434.0	1.2900	0.0000	0.0000	0.0000	0.0000

type dispersive forces leading to a positive contribution towards  $\Delta k_s$ ,  $H_m^E$  and negative contribution towards  $\Delta G^{*E}$  and  $\pi_i^E$ .

(ii) Chemical: Due to hydrogen bonding and other complex forming interaction making negative contribution towards  $\Delta k_s$ ,  $H_m^E$  and positive contribution towards  $\Delta G^{*E}$  and  $\pi_i^E$ .

(iii) Structural: Due to changes in interstitial accommodation, molar volume and free volume.

The sign and magnitude of deviation in isentropic

compressibility ( $\Delta k_s$ ) play an important role in assessing the molecular rearrangement as a result of molecular interaction between the component molecules in the liquid mixture. As can be seen from

Fig. 1,  $\Delta k_s$  is negative for DMSO+FA and positive for DMSO+DMF mixtures at all the three temperatures. As temperature is raised, an increase in the negative values of  $\Delta k_s$  and a decrease in positive values of  $\Delta k_s$  indicate that the molecular association becomes stronger with temperature. It has been suggested earlier<sup>19</sup> that liquids of different molecular size usually mix with negative

Table 3 — The values of coefficient  $a_i$  from Eq. (5) for  $\Delta k_s$ ,  $\pi_i^E$ ,  $\Delta G^{*E}$ ,  $H_m^E$  and standard deviation  $\sigma(Y^E)$  for binary mixtures at temperature  $T$ 

Functions	$a_0$	$a_1$	$a_2$	$\sigma(Y^E)$
DMSO + Formamide				
$T = 293$ K				
$\Delta k_s$ (Pa <sup>-1</sup> )	-0.4666	0.0370	0.3582	0.0038
$\pi_i^E$ (atm)	0.0683	-0.0688	0.1014	0.0005
$\Delta G^{*E}$ (kJ/mol)	3.6949	-0.8548	0.8605	0.0009
$H_m^E$ (j mol <sup>-1</sup> )	-40.2038	5.8992	-7.0360	0.0285
$T = 303$ K				
$\Delta k_s$ (Pa <sup>-1</sup> )	-0.6207	0.1149	0.2430	0.0033
$\pi_i^E$ (atm)	0.0964	-0.0600	0.0821	0.0004
$\Delta G^{*E}$ (kJ/mol)	4.0832	-0.7111	0.2280	0.0013
$H_m^E$ (j mol <sup>-1</sup> )	-37.9047	5.2488	-6.2493	0.0249
$T = 313$ K				
$\Delta k_s$ (Pa <sup>-1</sup> )	-0.9466	-0.2826	-0.5501	0.0020
$\pi_i^E$ (atm)	0.1737	-0.0070	0.0800	0.0001
$\Delta G^{*E}$ (kJ/mol)	4.2098	-0.7012	0.9265	0.0017
$H_m^E$ (j mol <sup>-1</sup> )	-37.9720	4.0194	-3.9623	0.0093
DMSO + N, N-dimethyl formamide				
$T=293$ K				
$\Delta k_s$ (Pa <sup>-1</sup> )	0.1792	0.0610	0.1810	0.0119
$\pi_i^E$ (atm)	-0.0347	-0.0099	-0.0051	0.0004
$\Delta G^{*E}$ (kJ/mol)	0.1597	-0.0726	-0.0196	0.0005
$H_m^E$ (j mol <sup>-1</sup> )	1.0051	0.8098	-0.3188	0.0305
$T = 303$ K				
$\Delta k_s$ (Pa <sup>-1</sup> )	0.1696	0.1034	-0.0454	0.0012
$\pi_i^E$ (atm)	-0.0247	-0.0042	-0.0060	0.0001
$\Delta G^{*E}$ (kJ/mol)	0.1147	-0.0607	-0.0139	0.0003
$H_m^E$ (j mol <sup>-1</sup> )	0.5456	0.3944	0.4704	0.0043
$T = 313$ K				
$\Delta k_s$ (Pa <sup>-1</sup> )	0.0635	0.0027	-0.1011	0.0046
$\pi_i^E$ (atm)	-0.0143	-0.0028	-0.0037	0.0002
$\Delta G^{*E}$ (kJ/mol)	0.2101	-0.0119	-0.0066	0.0002
$H_m^E$ (j mol <sup>-1</sup> )	-0.1054	0.2664	0.3092	0.0132

excess molar volume and deviation in isentropic compressibility ( $\Delta k_s$ ). The molar volumes for DMSO, FA and DMF at 293 K are 70.84 cm<sup>3</sup>/mol, 39.61 cm<sup>3</sup>/mol and 76.70 cm<sup>3</sup>/mol, respectively. The

The negative  $\Delta k_s$  values for DMSO+FA mixture indicate the presence of strong specific interactions, through hydrogen bonding between oxygen atom of DMSO (-S=O) and hydrogen atom of H – N – H group of FA molecules and due to filling of smaller

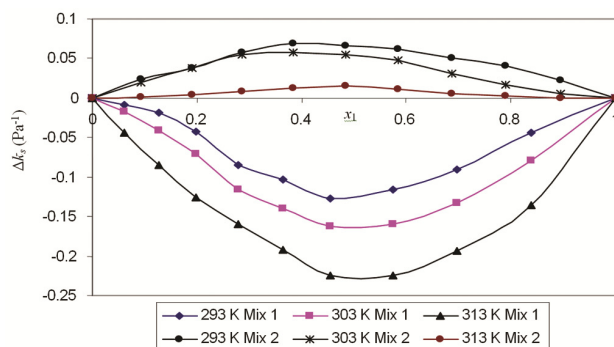


Fig. 1 — Deviation in isentropic compressibility ( $\Delta k_s$ ) against mole fraction of DMSO ( $x_1$ ) for (DMSO+FA) mixture (mix 1) and (DMSO+DMF) mixture (mix 2)

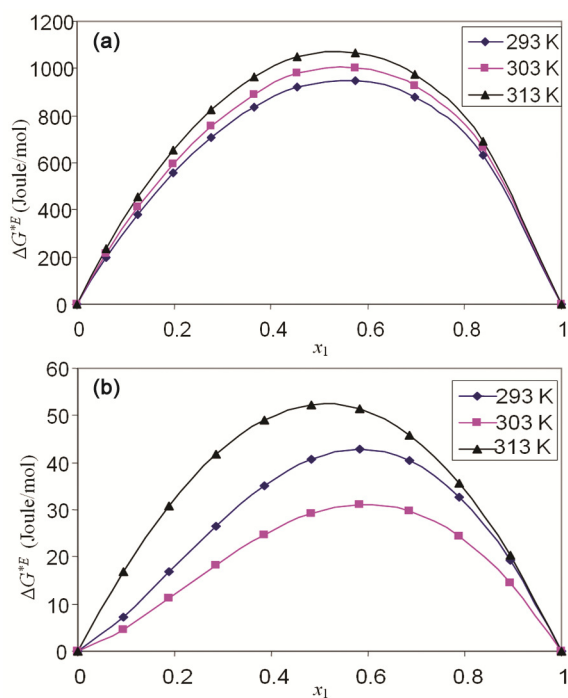


Fig. 2 — (a) Excess Gibbs free energy of activation ( $\Delta G^{*E}$ ) against mole fraction of DMSO ( $x_1$ ) for (DMSO+FA) mixture and (b) excess Gibbs free energy of activation ( $\Delta G^{*E}$ ) against mole fraction of DMSO ( $x_1$ ) for (DMSO+DMF) mixture.

molecule of FA into voids created by bigger molecules of DMSO. The positive values of  $\Delta k_s$  in the case of DMSO+DMF mixture can be explained on the basis of the fact that mixing of DMSO with DMF will induce the partial dissociation of dipolar association between DMSO-DMSO molecules, releasing several dipoles and it makes the mixture more compressible than the ideal mixture. The positive value of  $\Delta k_s$  may be attributed to the presence of weak interaction between the component

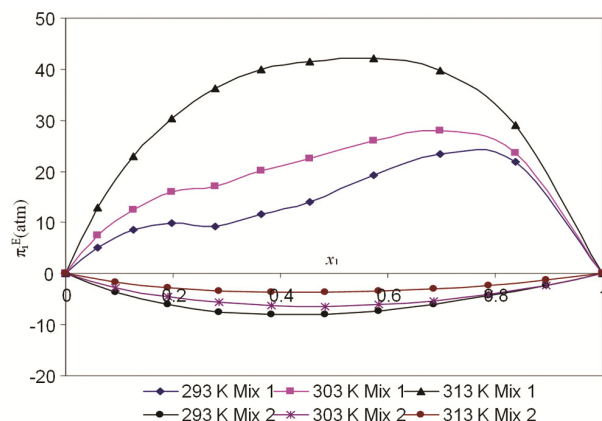


Fig. 3 — Excess internal pressure ( $\pi_i^E$ ) against mole fraction of DMSO ( $x_1$ ) for (DMSO+FA) mixture (mix 1) and (DMSO+DMF) mixture (mix 2).

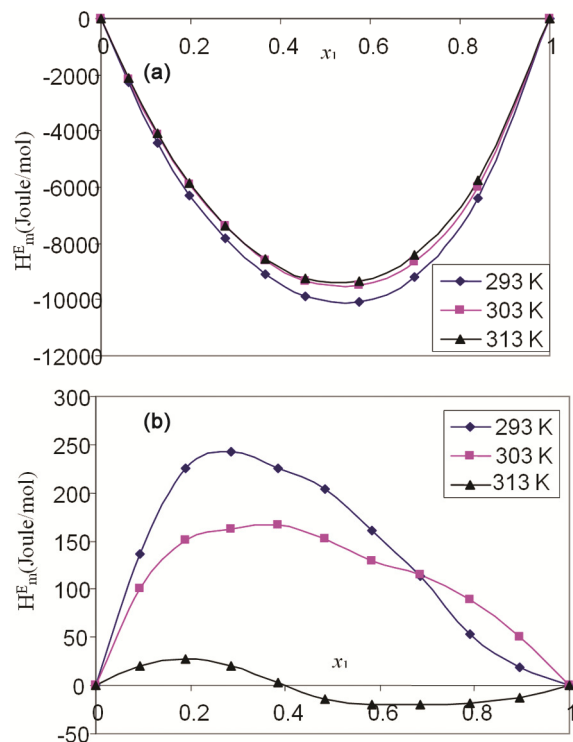


Fig. 4 — (a) Excess molar enthalpy ( $H_m^E$ ) against mole fraction of DMSO ( $x_1$ ) for (DMSO+FA) mixture and (b) excess molar enthalpy ( $H_m^E$ ) against mole fraction of DMSO ( $x_1$ ) for (DMSO+DMF) mixture.

molecules in the mixtures which in turn indicates the predominance of long range dispersive forces.

The apparent inter molecular interaction in DMSO+DMF mixture may be assigned from the weak dipole induced type forces resulting from the polarization of DMSO molecules by the dipoles of the

surrounding DMF molecules. This effect can be superimposed upon dipole–dipole interaction and lead to a slight increase in the attraction, giving less positive  $\Delta k_s$  values at higher temperature. These observations suggest that the specific interaction arising from induced dipole-dipole type force tend to increase with increasing temperature (Fig. 1). Similar trend in  $\Delta k_s$  values have also been reported for binary mixture of formamide with multi hydroxyl alcohols<sup>2</sup> and THF with alcohols<sup>13</sup>.

The variation of excess Gibb's free energy of activation with mole fraction for both the mixtures exhibit positive deviations. The positive value of  $\Delta G^{*E}$  is attributed to the presence of strong interaction between unlike molecule. Reed & Taylor<sup>20</sup> and Mayer *et al.*<sup>21</sup> suggested that the positive value of  $\Delta G^{*E}$  is an excellent indicator of strength of specific interactions between component molecules.  $\Delta G^{*E}$  curves are almost symmetrical around equimolar concentration in both the mixtures (Fig. 2). The more positive values of  $\Delta G^{*E}$  for DMSO+FA mixture might be due to some what better proton accepting ability of formamide than that of N,N-dimethylformamide. Also the steric hindrance of the two methyl groups of DMF, makes specific interaction comparatively weaker in DMSO+DMF mixture exhibiting less positive values of  $\Delta G^{*E}$  over the entire range of composition. Similar variations in  $\Delta G^{*E}$  values have also been reported earlier<sup>22</sup>. The positive value of  $\Delta G^{*E}$  has been found to increase with increase in temperature for both the mixtures. Increase in positive  $\Delta G^{*E}$  values with temperature suggests that thermal energy activates the molecules towards complex formation between unlike molecules.

As can be seen from Fig. 3, the values of  $\pi_i^E$  are positive for DMSO+FA mixture, which further indicates the existence of strong intermolecular

interaction in DMSO+FA mixture. The observed negative values of  $\pi_i^E$  for DMSO+DMF mixture over the entire composition range suggest that the loosening of dipolar interactions between DMSO molecules dominate over hydrogen bonding and interstitial accommodation as is also reflected by the values of  $\Delta k_s$ . The positive values of  $\pi_i^E$  increase with increase in temperature in the case of DMSO+FA mixture suggesting an increase in interaction due to the thermal energy. However in the case of DMSO+DMF mixture, less negative values of  $\pi_i^E$  are observed as temperature is raised. The increase in thermal energy decreases the self association of pure components. Similar temperature dependence has been reported by Marigliano *et al.*<sup>23</sup> for formamide+alcohol mixture.

Excess molar enthalpy  $H_m^E$  has been found to be negative for a DMSO + FA mixture and positive for DMSO + DMF mixtures (Fig. 4). The negative values of  $H_m^E$  in the case of DMSO+FA mixture indicate the presence of strong intermolecular interactions between unlike molecules. However the interaction between DMSO and DMF molecules may lead to weak dispersion type forces, giving rise to positive values in  $H_m^E$ . This may also be due to greater steric hindrance caused by two methyl group attached in the DMF molecule. Iloukhani and Zarei<sup>3</sup> have also found similar variation in  $H_m^E$  values with composition in binary mixture of DMF with alkanols. The variation of negative  $H_m^E$  values with temperature has been found to be insignificant in the case of DMSO+FA mixture. However positive  $H_m^E$  values in the case of DMSO+DMF mixture decrease as temperature increases and a change from positive to negative

Table 4 — Average percentage deviation (APD) of various theoretical mixing rules used for evaluation of ultrasonic velocity ( $u$ ) at varying temperatures

Temperatures (K)	Nomoto	Junjie	Vandael-Vangeel	CFT
DMSO +Formamide				
293	1.3060	1.3940	2.5850	0.7510
303	1.7067	1.8377	2.7688	1.0172
313	2.2860	2.4760	3.1153	1.4400
DMSO + N, N-dimethylformamide				
293	-0.5609	-0.3551	-0.5252	-0.6115
303	-0.4223	-0.2060	-0.3858	-0.4737
313	-0.1577	0.0023	-0.1233	-0.1972

in DMSO rich region suggests decrease in self association of the pure component and an increase in strength of interaction with temperature.

The theoretical values of ultrasonic velocities in both the mixtures were calculated using the relations described earlier<sup>24</sup>. The APD values using different relation for both the mixtures are presented in Table 4. It is observed that collision factor theory (CFT) provides comparatively better results with minimum APD of 0.7510 in the case of DMSO+FA mixture. However, in the case of DMSO+DMF all the relations exhibit excellent results with minimum APD of 0.0023 for Junjie's relation and maximum APD of 0.6115 for CFT. The applicability of these relations in predicting experimental ultrasonic velocity for polar-polar mixtures has also been recognized by others<sup>25,26</sup>.

## 5 Conclusions

The observed positive and negative values of various excess parameters suggest the existence of strong hydrogen bonding between unlike molecules in the case of DMSO+FA mixtures. However weak dipole-dipole interaction and dispersive forces seem to be predominant in DMSO+DMF mixtures. A good agreement has been found between experimental and theoretical values of ultrasonic velocity.

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