

Ultrasonic Speeds and Isentropic Compressibility for Binary Mixtures of DMSO with Alkanols

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Measurement of ultrasonic speed have been carried out on binary mixtures of DMSO with *n*-alkanol (C₆, C₇, C₈, C₁₀) at 313.15 K over the entire mole fraction range. Ultrasonic velocity values have been used to calculate the values of isentropic compressibility K_s, Rao's constant W, intermolecular free length L_f, Van der Waals' constant b, solvation number S_n, and excess free volume V_f^E. A qualitative discussion of the results is presented.

INTRODUCTION

In continuation of our earlier work on ultrasonics^{1,2}, we report in the present paper the measured ultrasonic velocity *u* values for the binary mixtures of DMSO with alkanols (C₆, C₇, C₈, C₁₀) over the whole mole fraction range at 313.15 K. The *u* values have been used to calculate excess isentropic compressibility K_s^E, Rao's constant³ R, specific acoustic impedance Z, Wada's constant⁴ W, intermolecular free length L_f, Van der Waals constant⁵ b, solvation number S_n and free volume⁶ V_f.

The experimental ultrasonic velocity values have also been compared with theoretical values calculated, at different concentrations, using the concept of Flory's^{7,8} theory, Jacobson's free length⁹ theory, Schaaffs¹⁰ collision factor theory, Junjie's¹¹ empirical relation and Nomoto's¹² equation.

EXPERIMENTAL

Ultrasonic velocities were measured using a single crystal interferometer at a frequency of 2 MHz. The details of experimental procedure have been described elsewhere¹.

The densities of binary mixtures required for the computation of various parameters have been calculated from excess volumes V^E data reported earlier¹³.

The alkanols and quinoline used in the present work are the same as in earlier studies¹³. All the chemicals were dried over freshly activated molecular sieves (IDPL Tpye 4A) before use.

THEORETICAL

Isentropic compressibility K_s, free volume V_f, specific acoustic impedance Z, solvation number S_n, relative association R_A, molecular association M_A, Rao's constant R, Wada's constant W, intermolecular free length L_f and Van der Waals' constant b of a binary mixture are calculated

from measured ultrasonic velocity u and density ρ by using the following relations

$$K_s = 1/u^2\rho \quad (1)$$

$$V_f = V(u_g/u)^3 \quad (2)$$

$$Z = u \cdot \rho \quad (3)$$

$$S_n = (n_1/n_2)\{1 - (K_s/K_{s,1})\} \quad (4)$$

$$R_A = (L_f/L_f')^3 \quad (5)$$

$$M_A = \{(u^2/u_{im}^2) - 1\} \quad (6)$$

$$R = \bar{M}u^{1/3}/\rho \quad (7)$$

$$W = \bar{M}K_s^{-1/7}/\rho \quad (8)$$

$$L_f = K(K_s)^{1/2} \quad (9)$$

$$b = (M/\rho) - (RT/\rho u^2)[\{1 + (Mu^2/3RT)\}^{1/2} - 1] \quad (10)$$

where u_g and u_{im} are the ultrasonic velocity in the vapour phase and of ideal mixture, n_1 , n_2 are the number of moles of the respective components, L_f the free length of the ideal mixing and M is the average molecular weight. K is a temperature dependent constant.

The deviations from linear dependence of isentropic compressibility on mole fraction are obtained from the relations

$$K_s^E = K_s - K_s^{id} \quad (11)$$

where K_s^{id} is defined as

$$K_s^{id} = (\sum \psi_i \gamma_i K_{s,i}) \{ \sum x_i (C_{p,i} / \gamma_i) / \sum x_i C_{pi} \}$$

where $\lambda_i = [1 + (TV_i \alpha_{pi}^2 / K_{s,i} C_{p,i})]$ and $C_{p,i}$, $\alpha_{p,i}$ are the isobaric molar heat capacity and thermal expansibility for the pure component i . On substituting value of γ_i in eq. (12)

$$K_s^{id} = \sum \phi_i (K_{s,i} + TV_i \alpha_{p,i}^2 / C_{p,i}) - [T(\sum x_i V_i)(\sum \phi_i \alpha_{p,i})^2 / (\sum x_i C_{p,i})] \quad (13)$$

The volume fraction ϕ is defined as

$$\phi_i = x_i V_i / \sum x_i V_i \quad (14)$$

For comparison, the theoretical values of ultrasonic velocities u are computed using three theories and two empirical equations

Flory's theory ; $u = (\sigma/6.3 \cdot 10^{-4} \rho)^{2/3}$

Collision factor theory : $u = u_\infty (x_1 S_2 + x_2 S_2) \{ (x_1 B_1 + x_2 B_2) / V \}$

Free length theory : $u = K / (L_f \cdot \rho^{1/2})$

Junjie's equation : $u = \{ (x_1 M_1 / \rho_1) + (x_2 M_2 / \rho_2) \} / [(x_1 M_1 + x_2 M_2)^{1/2} \cdot \{ (x_1 M_1 / \rho_1^2 u^2) + (x_2 M_2 / \rho_2^2 u^2) \}^{1/2}]$

Nomoto equation : $u = \{ (x_1 R_1 + x_2 R_2) / (x_1 V_1 + x_2 V_2) \}^3$

Reference should be made to our earlier paper² for details of the derivations and symbols.

RESULT AND DISCUSSION

Ultrasonic velocity u and related parameters *viz.* K_s , Z , W , R , L_f , b , V_f , V_a , RA , MA and S_n for pure components and all the mixtures containing DMSO are presented in Tables 1 and 2 as a function of x . The calculated parameters (K_s , S_n , L_f , Z , b , R , W) vs x curves for DMSO(x) + n -alkanols ($1 - x$) mixtures are shown in Fig. 1.

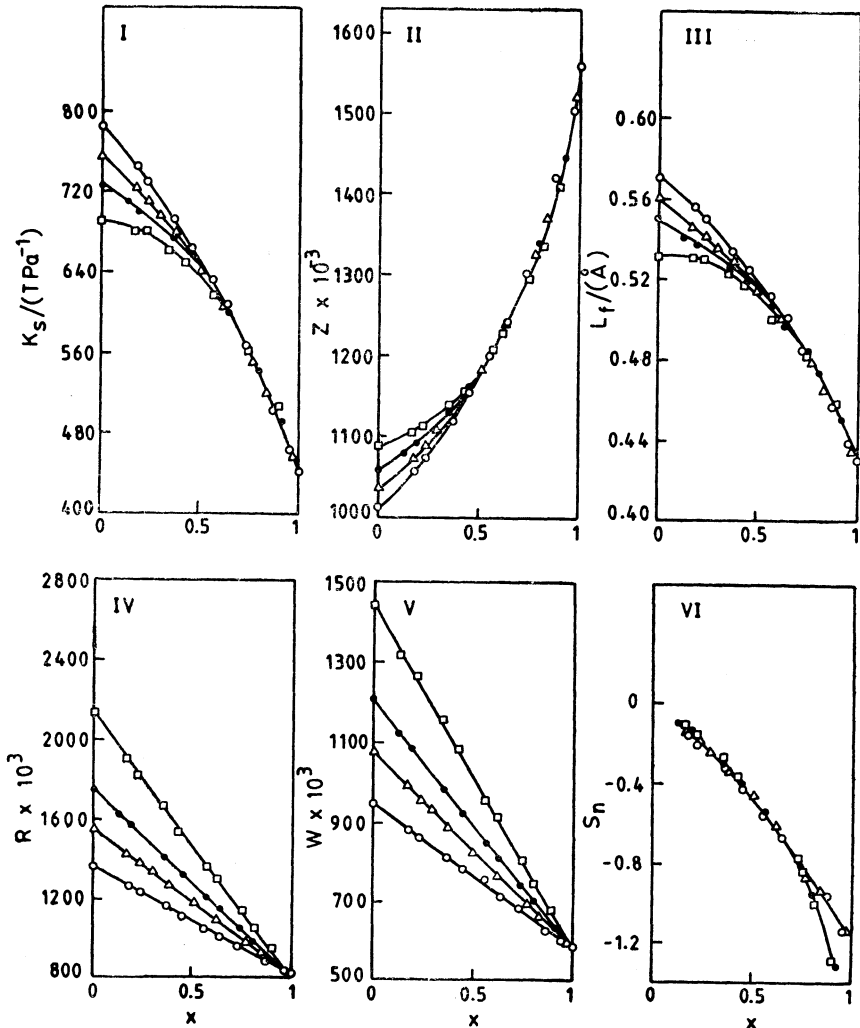


Fig. 1. Isentropic compressibility K_s , intermolecular free length L_f , specific acoustic impedance Z , Rao's constant R , Wada's constant W and solvation number S_n for \circ , $\{x(\text{CH}_3)_2\text{SO} + (1-x)\text{C}_6\text{H}_{13}\text{OH}\}$; \triangle , $\{x(\text{CH}_3)_2\text{SO} + (1-x)\text{C}_7\text{H}_{15}\text{OH}\}$; \bullet , $\{x(\text{CH}_3)_2\text{SO} + (1-x)\text{C}_8\text{H}_{17}\text{OH}\}$; \square , $\{x(\text{CH}_3)_2\text{SO} + (1-x)\text{C}_{10}\text{H}_{21}\text{OH}\}$.

TABLE I
VALUES OF ULTRASONIC VELOCITIES AND THE OTHER DERIVED PARAMETERS OF THE PURE COMPONENTS

	u ($m \cdot s^{-1}$)	K_s (TPa $^{-1}$)	$^a Z \times 10^4$	V_t ($cm^3 \cdot mol^{-1}$)	$b \times 10^6$ (m^2)	r (nm)	B ($cm^3 \cdot mol^{-1}$)	$Y \times 10^4$ ($cm^2 \cdot mol^{-1}$)	s	V_s ($cm^3 \cdot mol^{-1}$)	L_t (\AA°)	L_t (\AA°)	RA	$^b R \times 10^3$	$^c W \times 10^3$	u_{RT} ($m \cdot s^{-1}$)	u_{RT} ($m \cdot s^{-1}$)
<i>n</i> -Hexanol	1258	785.9	1011	0.262	119.60	0.228	29.90	39.35	3.34	27.17	0.569	0.552	1.094	1371	946	1296	1419
<i>n</i> -Heptanol	1279	756.1	1034	0.218	135.78	0.238	33.95	42.82	3.38	28.83	0.558	0.538	1.120	1560	1076	1328	1433
<i>n</i> -Octanol	1303	726.1	1056	0.196	152.20	0.247	38.05	46.21	3.44	29.80	0.547	0.565	0.909	1753	1209	1262	1448
<i>n</i> -Decanol	1331	691.8	1086	0.136	184.84	0.264	46.21	52.60	3.49	32.61	0.534	0.489	1.304	2133	1471	1454	1487
DMSO	1443	444.4	1559	0.162	68.05	0.189	17.01	27.02	3.83	7.09	0.428	0.369	1.558	817	584	1673	1455

$^a Z = (m \cdot s^{-1})(Kg \cdot m^{-2})$
 $^b R = (m \cdot s^{-1})^{1/2}(m^3 \cdot mol^{-1})$
 $^c W = (m^3 \cdot mol^{-1})(TPa^{-1})^{1/2}$

TABLE 2
ULTRASONIC VELOCITY DATA BINARY MIXTURES AT 313.15 K

x_2	u (m·s ⁻¹)	ρ (kg·m ⁻³)	K_s (TPa ⁻¹)	K_s^* (TPa ⁻¹)	V_t (cm ³ ·mol ⁻¹)	V_t^* (cm ³ ·mol ⁻¹)	V_s (cm ³ ·mol ⁻¹)	L_t^* (Å°)	L_t (Å°)	RA	MA	$b \times 10^6$ (m ³)	$Z \times 10^{-3}$	$R \times 10^3$	$W \times 10^3$	S_2
0.1845	1267	834.1	746.8	-0.6	0.261	0.017	24.388	0.532	0.555	1.135	-0.0308	110.19	1056	1267	879	-0.15
0.2365	1273	843.7	731.4	-3.8	0.258	0.020	23.374	0.525	0.549	1.144	-0.0344	107.54	1074	1239	860	-0.20
0.3674	1288	870.1	692.8	-9.1	0.250	0.024	20.919	0.507	0.534	1.168	-0.0445	100.85	1120	1167	813	-0.32
0.4570	1298	890.5	666.5	-9.7	0.243	0.027	19.327	0.493	0.524	1.201	-0.0525	96.24	1155	1116	780	-0.42
0.5610	1310	917.1	635.4	-7.6	0.235	0.029	17.529	0.475	0.512	1.252	-0.0620	90.88	1201	1058	742	-0.55
0.6415	1321	940.1	609.6	-5.0	0.228	0.030	16.092	0.460	0.501	1.292	-0.0674	86.71	1241	1012	712	-0.67
0.7304	1346	968.5	569.9	-9.7	0.213	0.024	13.870	0.441	0.485	1.330	-0.0562	82.11	1303	964	681	-0.77
0.8758	1390	1023.3	505.8	-7.3	0.187	0.013	10.404	0.405	0.457	1.437	-0.0359	74.54	1422	884	628	-0.97
0.9585	1422	1060.2	466.4	-2.4	0.171	0.005	8.303	0.382	0.438	1.507	-0.0162	70.22	1507	839	598	-1.14
$x(\text{CH}_3)_2\text{SO} + (1-x)\text{C}_7\text{H}_{15}\text{OH}$																
0.1737	1287	833.2	724.6	-2.2	0.226	0.018	25.729	0.522	0.546	1.144	-0.0171	124.12	1072	1430	991	-0.13
0.2414	1291	844.2	710.7	-3.1	0.228	0.024	24.481	0.515	0.541	1.159	-0.0236	119.58	1089	1380	957	-0.19
0.2961	1296	853.7	697.4	-5.1	0.228	0.027	23.351	0.509	0.536	1.168	-0.0266	115.90	1106	1339	931	-0.24
0.3816	1301	870.1	679.0	-4.3	0.229	0.033	21.837	0.499	0.529	1.191	-0.0365	110.14	1131	1275	888	-0.33
0.5108	1317	898.6	641.6	-8.4	0.225	0.035	19.044	0.481	0.514	1.220	-0.0412	101.42	1183	1180	825	-0.46
0.6275	1332	929.4	606.5	-8.0	0.218	0.035	16.637	0.461	0.500	1.276	-0.0473	93.51	1237	1092	767	-0.61
0.7769	1359	977.9	553.7	-5.2	0.204	0.029	13.342	0.431	0.478	1.364	-0.0482	83.34	1329	981	693	-0.86
0.8396	1380	1002.4	523.9	-7.4	0.193	0.022	11.555	0.416	0.465	1.397	-0.0367	79.07	1383	935	663	-0.94
0.9715	1430	1064.7	459.3	-2.5	0.168	0.004	7.905	0.379	0.435	1.512	-0.0084	70.02	1522	838	598	-1.14

TABLE 2 (contd.)

$x(\text{CH}_3)_2\text{SO} + (1-x)\text{C}_{10}\text{H}_{17}\text{OH}$																
0.1331	1304	827.6	710.6	2.3	0.209	0.017	27.562	0.552	0.541	0.941	-0.0065	141.07	1079	1627	1125	-0.09
0.1952	1307	836.2	700.1	1.2	0.212	0.023	26.294	0.545	0.537	0.957	-0.0074	135.89	1092	1569	1087	-0.14
0.3603	1312	862.8	674.4	3.2	0.222	0.038	23.254	0.525	0.527	1.011	-0.0200	122.08	1131	1414	983	-0.29
0.4502	1318	880.1	654.1	2.6	0.223	0.043	21.382	0.512	0.519	1.042	-0.0255	114.55	1160	1330	927	-0.39
0.5703	1330	907.6	622.9	0.7	0.221	0.045	18.689	0.491	0.507	1.101	-0.0312	104.46	1207	1217	852	-0.53
0.6370	1340	925.5	601.7	-1.5	0.217	0.043	17.039	0.478	0.498	1.131	-0.0317	98.86	1240	1155	811	-0.62
0.7462	1354	960.1	568.1	1.1	0.210	0.039	14.630	0.452	0.484	1.228	-0.0396	89.62	1299	1052	742	-0.82
0.8080	1365	983.3	545.8	2.8	0.203	0.034	13.165	0.436	0.474	1.285	-0.0418	84.38	1342	994	703	-0.96
0.9214	1398	1035.1	494.3	4.3	0.184	0.019	10.029	0.399	0.451	1.444	-0.0327	74.74	1447	888	632	-1.32
$x(\text{CH}_3)_2\text{SO} + (1-x)\text{C}_{10}\text{H}_{11}\text{OH}$																
0.1698	1327	833.4	681.4	7.1	0.154	0.014	29.622	0.482	0.530	1.329	0.0202	165.09	1105	1907	1319	-0.11
0.2268	1322	840.2	681.0	13.5	0.165	0.023	28.974	0.480	0.530	1.346	0.0165	158.45	1110	1830	1267	-0.16
0.3564	1326	858.2	662.7	13.0	0.183	0.038	25.884	0.473	0.523	1.352	0.0232	143.39	1138	1660	1153	-0.27
0.4371	1327	871.7	651.5	15.0	0.193	0.046	24.125	0.467	0.518	1.365	0.0188	133.99	1156	1553	1081	-0.36
0.5793	1340	901.0	618.1	9.8	0.202	0.051	20.172	0.454	0.505	1.376	0.0165	117.43	1207	1368	956	-0.54
0.6275	1347	913.1	603.6	6.8	0.203	0.051	18.701	0.448	0.499	1.382	0.0160	111.81	1229	1306	914	-0.60
0.7538	1363	951.7	565.6	5.1	0.202	0.046	15.231	0.430	0.483	1.417	0.0020	97.05	1297	1140	802	-0.83
0.8154	1370	975.5	546.1	7.7	0.199	0.042	13.693	0.419	0.474	1.448	-0.0110	89.81	1336	1057	747	-1.01
0.8972	1390	1014.4	510.2	7.1	0.188	0.029	11.175	0.401	0.459	1.500	-0.0185	80.19	1410	950	674	-1.29

TABLE 3

REDUCTION AND CHARACTERISTIC PARAMETERS OF THE PURE COMPONENTS 313.15 K

Component	$^a\alpha \times 10^{-4}$ (K ⁻¹)	bK_T (TPa ⁻¹)	\bar{v}	V (cm ³ ·mol ⁻¹)	V^* (cm ³ ·mol ⁻¹)	T^* (K)	P^* (J·cm ⁻³)
<i>n</i> -Hexanol	9.203	921.19	1.2408	127.09	102.42	5599	481.67
<i>n</i> -Heptanol	8.905	892.04	1.2343	143.72	116.44	5704	476.25
<i>n</i> -Octanol	9.245	868.71	1.2417	160.54	129.29	5584	513.85
<i>n</i> -Decanol	8.578	807.11	1.2270	193.98	158.09	5828	501.10
DMSO	9.254	559.14	1.2419	72.30	58.22	5581	799.38

^aCalculated using literature densities.^bCalculated using ultrasonic velocity values.

TABLE 4

COMPARISON OF PERCENTAGE ERRORS FOR THE ULTRASONIC VELOCITY OF BINARY MIXTURES

Mixture	Error (%)				
	u_F ms ⁻¹	u_{CPT} ms ⁻¹	u_{FLT} ms ⁻¹	u_j ms ⁻¹	u_N ms ⁻¹
DMSO					
+ <i>n</i> -hexanol	8.49	2.60	9.02	0.67	1.34
+ <i>n</i> -heptanol	8.21	2.37	8.87	0.57	1.08
+ <i>n</i> -octanol	7.68	2.94	6.06	0.17	1.57
+ <i>n</i> -decanol	8.69	3.20	11.64	0.60	1.82

Error = $[\sum\{100(u_{exp} - u_{cal})/u_{exp}\}^2/N]^{1/2}$, where N is the number of data points.

As reported earlier¹³, V^E values are positive for all the mixtures of DMSO with alkanols and decrease in the order *n*-decanol > *n*-octanol > *n*-heptanol > *n*-hexanol. The K_s^E values for DMSO + *n*-decanol, and + *n*-octanol are positive over the whole range of composition but become negative as *n*-heptanol or *n*-hexanol is substituted for these alkanols. It may, therefore, be inferred that the trend followed by V^E and K_s^E is the same.

The values of u and Z increase with increasing x of DMSO for all the four systems (Table 2) while K_s , L_f and S_n behave in the reverse order. The data do not exhibit any sudden variation in u and K_s (Fig. 1),

thereby implying the absence of complex formation, which is again supported by linear variation of R , W , and b parameters.

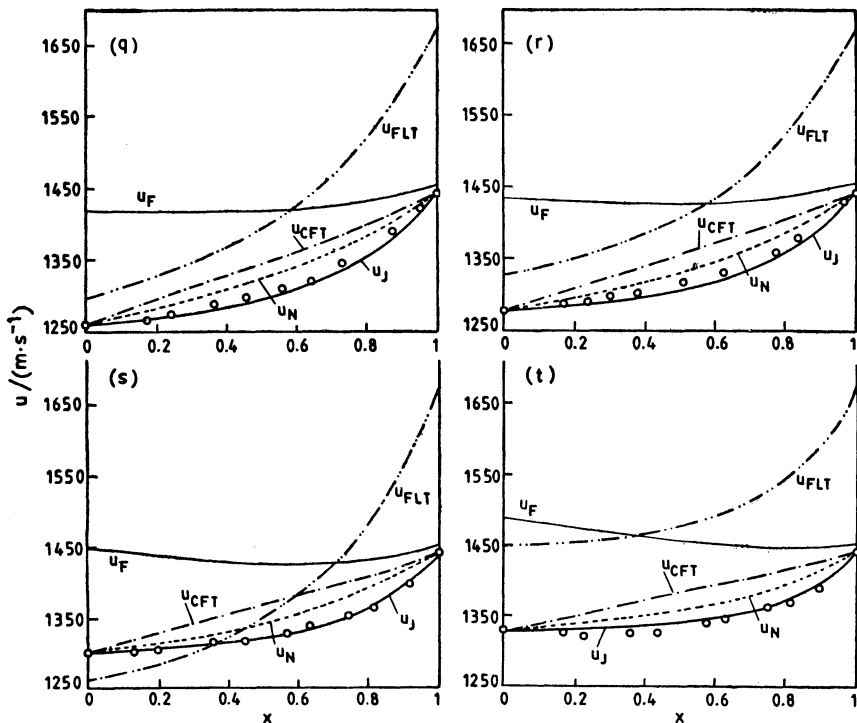


Fig. 2. Experimental and calculated ultrasonic velocities $u(\circ\circ\circ)$, u_F (—), u_{FLT} (- - - - -), u_{CFT} (- · - · -), u_J (— — — —), u_N (- - -) for (q), $\{x(\text{CH}_3)_2\text{SO} + (1-x)\text{C}_6\text{H}_{13}\text{OH}\}$; (r), $\{x(\text{CH}_3)_2\text{SO} + (1-x)\text{C}_7\text{H}_{15}\text{OH}\}$; (s), $\{x(\text{CH}_3)_2\text{SO} + (1-x)\text{C}_8\text{H}_{17}\text{OH}\}$; (t), $\{x(\text{CH}_3)_2\text{SO} + (1-x)\text{C}_{10}\text{H}_{21}\text{OH}\}$,

The increasing trend of the relative association RA with increase in x of DMSO signifies that the AB interactions in these mixtures may be strongly associative. Further, the maximum and minimum deviation in MA are observed in the case of DMSO + n -hexanol and DMSO + n -decanol respectively. It may, therefore, be concluded that DMSO forms the most non-ideal mixture with hexanol and that the nonideality of the mixtures formed decreases as the chain length of the alkanol added increases. The values of V_f^E , like V^E , are positive for all the mixtures.

Ultrasonic velocities for all the binary mixtures have been calculated theoretically at different concentrations using Flory's theory, Schaaffs Collision factor theory (CFT) and Jacobson's Free length theory (FLT). The average percentage error of computed u_F , u_{FLT} and u_{CFT} values in comparison to experimental values for all the mixtures are summarized in Table 4. The two empirical equations as proposed by Junjie and

Nomoto have also been used to compute the ultrasonic velocities of all the binary mixtures. The average percentage errors obtained for these cases have also been included in Table 4.

A close scrutiny of the results indicates that the collision factor theory does succeed in computing the ultrasonic velocity values for all the mixtures studied in the present investigation whereas the error range in the case of Flory's theory and Free length theory is quite large. Both Junjie and Nomoto's expressions fit the experimental data reasonably well.

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