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Speeds of sound and isentropic compressibilities of mixtures containing dipropylene glycol monomethyl ether and n-alkanols at 298.15 K

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Abstract Speeds of sound have been measured for binary mixtures of dipropylene glycol monomethyl ether with methanol, 1-propanol, 1-pentanol, and 1-heptanol, as a function of composition, at 298.15 K. The values have been combined with those of densities derived from excess molar volumes to obtain estimates of the product $K_{s,m}$ of the molar volumes and isentropic compressibility κ_s, and excess quantity $K^E_{s,m}$. The $K^E_{s,m}$ values are negative over the entire range of composition for all mixtures. The magnitude of $K^E_{s,m}$ increases with the number of carbon atoms in the *n*-alcohol. The deviation of the speeds of sound u^D from their values in an ideal mixture were also evaluated for all measured mole fractions. These values are compared with the mixing function δu calculated in the paper. The behaviour of u^D, δu, and $K^E_{s,m}$ with composition and the number of carbon atoms in the alcohol molecule is discussed.

Keywords Binary liquid mixtures, acoustical parameters, molecular interactions

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1. Introduction

In an earlier paper [1], we have reported the results of our measurements of the excess molar volumes of dipropylene glycol monomethyl ether with n-alcohol at 298.15 K. These results suggested structural changes of dipropylene glycol monomethyl ether by alcohol molecules. Since the study of ultrasonic speed and isentropic compressibility in binary liquid mixtures are of considerable interest [2–5] in assessing the nature of molecular interactions and investigating the physico-chemical behaviour of liquid systems, we thought worthwhile to perform measurements of the speed of sound for these mixtures in order to evaluate various thermodynamic properties and functions that give a better understanding of the molecular interactions existing between alkoxyethanol and alkanols. Hence, we report here measured values of speeds of sound in (dipropylene glycol monomethyl ether + methanol, 1-propanol, 1-pentanol, and 1-heptanol) at 298.15 K and atmospheric pressure. The isentropic compressibilities κ_s for all mixtures were estimated by combining the densities derived from excess molar volumes [1] and the speeds of sound. The molar volume were multiplied by the isentropic compressibilities to obtain estimates of $K_{s,m}$. We have also calculated the deviations u^D of the speeds of sound from those in the ideal mixture u^{id}, together with the mixing function δu and the excess molar quantities $K^E_{s,m}$.

2. Experimental

Dipropylene glycol monomethyl ether (Merck-Schuchardt, FRG, GC, mass fraction >95) was used without further purification. Spectroscopic grade alcohols were dried and fractionally distilled as described elsewhere [6]. All samples were kept in tightly sealed bottles to minimize the absorption of atmospheric moisture and CO_2, and dried over 0.4 nm molecular sieves to reduce water content. Prior to measurements, all liquids were partially degassed at low pressure. The purities of the liquids were checked by measuring their densities with a bicapillary pycnometer of about 10 cm^3 capacity. The measurements at 298.15 ± 0.01 K have an estimated reproducibility of 0.3 kg m^{-3}. The values obtained for densities were compared with the literature data [6–14] in Table 1. Also given in Table 1 are our measured or literature values of those quantities which are required in the estimation of $\kappa_{s,m}$, $K^E_{s,m}$ and u^D. Binary

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Table 1. Observed and literature values of densities (ρ^*), isobaric thermal expansivities (α_p^*), molar isobaric heat capacities ($C_{p,m}^*$), ultrasonic speeds (u^*), and the product $K_{s,m}^*$ of the molar volume and isentropic compressibility of pure liquid components at 298.15 K

Component	ρ^* (kg m^{-3}) obs		α_p^* (kK^{-1})	$C_{p,m}^*$ (J K mol^{-1})	u^* (m s^{-1}) obs	lit.	$K_{s,m}^*$ (mm^3 mol^{-1} MPa^{-1})
Dipropylene glycol monomethyl ether	952.7		0.242[a]	294.6[b]	1303.1		618.14
Methnaol	786.4	786.54 [6] 786.38 [7] 786.61 [8]	1.201 [9]	81.21 [7]	1100.6	1101.80 [8] 1102 [10]	1049.78
1-Propanol	799.4	799.50 [7] 799.35 [9]	1.003 [9]	144.10 [7]	12.04.6	1205.17 [8]	862.09
1-Pentanol	811.1	811.15 [6] 811.10 [8]	0.893 [11]	208.4 [12]	1273.9	1275.18 [8]	759.72
1-Heptanol	819.2	819.50 [13] 818.9 [14]	0.845[b]	271.7[a]	132.7		692.49

[a]estimated using group additivity, [b]calculated from our measured densities

mixtures were prepared by mass at room temperature with a precision of ± 0.05 mg. Corrections were made for buoyancy. The composition of each mixture was obtained with an accuracy of 1×10^{-4} from the measured apparent masses of the components. All molar quantities were based upon the IUPAC table of atomic weights [15].

The speeds of sound in both the pure liquids and their mixtures were measured at 4 MHz using NUSONIC (Mapco, Model, 6080 Concentration Analyzer) velocimeter based on sing-around technique [16] with a single transducer cell. The ultrasonic speeds at 298.15 K are directly obtained from the average round trip period of the ultrasonic wave in a fixed path length between the piezoelectric transducer and reflector. The maximal error of the speed measured relative to water (1496.687 m s^{-1} at 298.15 K) [17] is estimated to be less than 0.2 m s^{-1}. Further details concerning this apparatus, experimental set-up and operational procedures have been described in our previous work [18,19]. A thermostatically controlled, well stirred water bath whose temperature was controlled to ±0.01 K, was used for all measurements.

3. Results and discussion

Table 2 gives the experimental results of speed of sound at 298.15 K of all the binary mixtures at various mole fractions. Also listed there are deviations u^D of the ultrasonic speed from the values u^{id} calculated for ideal mixtures, the product $K_{s,m}$ of the molar volume and the isentropic compressibility, and their corresponding excess molar quantity $K_{s,m}^E$.

The κ_s and $K_{s,m}$ have been calculated from the relation:

$$\kappa_s = (\rho \cdot u^2)^{-1} = V_m (M \cdot u^2)^{-1}, \quad (1)$$

$$K_{s,m} = -(\partial V_m / \partial p)_s = V_m \cdot \kappa_s = V_m^2 / (M \cdot u^2), \quad (2)$$

where ρ is the density and $M = \Sigma x_i M_i^*$ is the molar mass of the mixture.

Table 2. Ultrasonic speeds u, deviations u^D from ultrasonic speed in an ideal mixture, u^{id}, the product $K_{s,m}$ of the molar volume and isentropic compressibility, and the corresponding excess quantity $K_{s,m}^E$ for liquid mixtures at 298.15 K

x	u (m s^{-1})	u^D (m s^{-1})	$K_{s,m}$ (mm^3 mol^{-1} MPa^{-1})	$K_{s,m}^E$ (mm^3 mol^{-1} MPa^{-1})
		xCH$_3$[O(CH$_2$)$_3$]$_2$OH + (1 − x)CH$_3$OH		
0.0013	1101.9	1.09	42.77	−0.09
0.0024	1103.3	2.30	42.75	0.19
0.0037	1104.6	3.38	42.76	−0.29
0.0057	1106.2	4.63	42.79	−0.40
0.0072	1107.6	5.77	42.80	−0.49
0.0092	1109.3	7.11	42.83	−0.61
0.0117	1111.2	8.55	42.88	−0.74
0.0219	1119.1	14.47	43.08	−1.27
0.0356	1129.3	21.79	43.37	−1.93
0.0522	1141.2	29.93	43.74	−2.68
0.0749	1156.0	39.23	44.35	3.57
0.0992	1169.9	46.92	45.13	−4.35
0.1327	1186.1	54.25	46.38	−5.17
0.1723	1203.5	60.99	47.93	−5.99
0.1992	1213.2	63.46	49.11	−6.37
0.2482	1229.4	66.69	51.32	−6.94
0.2873	1240.0	67.22	53.21	−7.21
0.3246	1248.7	66.59	55.10	−7.34
0.3509	1254.1	65.59	56.47	−7.38
0.3910	1261.4	63.44	58.63	−7.35
0.4378	1268.8	60.27	61.20	−7.21
0.4792	1274.2	56.72	63.56	−6.98
0.5303	1280.0	51.99	66.53	−6.61
0.5716	1284.5	48.37	68.93	−6.29
0.6069	1287.5	44.71	71.05	−5.94
0.6336	1289.4	41.72	72.69	−5.63
0.6540	1291.0	39.68	73.93	−5.41
0.6796	1292.5	36.71	75.53	−5.08
0.7414	1294.2	28.10	79.60	−4.04
0.7754	1295.6	24.09	81.78	−3.52
0.8071	1297.1	20.71	83.78	−3.06
0.8406	1298.3	19.91	85.94	−2.54
0.8762	1299.6	13.08	88.21	−1.99
0.8959	1300.2	10.91	89.48	−1.67

Table 2. (Cont'd.)

x	u (m s^{-1})	u^D (m s^{-1})	$K^*_{s,m}$ (mm^3 mol^{-1} MPa^{-1})	$K^E_{s,m}$ (mm^3 mol^{-1} MPa^{-1})
0.9156	1301.4	9.39	90.66	−1.44
0.9309	1301.6	7.52	91.68	−1.16
0.9507	1302.0	5.27	92.97	−0.82
0.9631	1302.3	3.94	93.77	−0.61
0.9717	1302.5	3.02	94.33	−0.47
0.9849	1302.8	1.62	95.18	−0.26
0.9929	1302.9	0.70	95.70	−0.11
0.9970	1303.0	0.28	95.97	−0.04
		xCH$_3$[O(CH$_2$)$_3$]$_2$OH + (1 − x)C$_3$H$_7$OH		
0.0007	1204.7	0.11	64.83	−0.01
0.0015	1204.9	0.32	64.84	−0.04
0.0029	1205.2	0.63	64.86	−0.07
0.0039	1206.1	1.55	64.81	−0.17
0.0055	1206.9	2.36	64.79	−0.26
0.0077	1207.1	2.58	64.86	−0.29
0.0116	1208.1	3.31	64.92	−0.41
0.0294	1212.1	7.61	65.23	0.88
0.0389	1214.2	9.63	65.40	−1.11
0.0495	1216.3	11.57	65.63	1.35
0.0642	1219.3	14.25	65.93	−1.67
0.0819	1222.7	17.12	66.31	−2.02
0.0980	1225.7	19.50	66.67	−2.31
0.1230	1230.3	22.93	67.23	−2.74
0.1562	1235.8	26.50	68.05	−3.21
0.1986	1242.5	30.23	69.13	−3.72
0.2436	1249.4	33.46	70.28	−4.18
0.2794	1252.3	33.14	71.50	−4.21
0.3433	1260.0	34.54	73.37	−4.48
0.3954	1265.7	34.72	74.95	4.58
0.4471	1270.5	33.77	76.61	−4.53
0.4867	1273.9	32.64	77.91	−4.43
0.5236	1276.8	31.23	79.15	−4.29
0.5593	1279.9	30.11	80.30	−4.18
0.5889	1282.0	28.67	81.32	−4.01
0.6283	1284.4	29.69	82.58	−3.78
0.6832	1287.9	23.17	84.63	−3.33
0.7316	1290.7	20.08	86.35	−2.92
0.7808	1293.3	16.71	88.11	2.46
0.8256	1296.0	13.92	89.69	−2.07
0.8593	1297.3	11.13	90.96	1.67
0.8920	1298.6	8.47	92.18	−1.28
0.9196	1299.7	6.23	93.21	−0.95
0.9347	1300.5	5.22	93.74	−0.79
0.9469	1301.3	4.55	94.15	−0.69
0.9573	1301.5	3.50	94.57	−0.53
0.9731	1302.0	2.11	95.17	−0.32
0.9887	1302.5	0.75	95.76	−0.12
0.9945	1302.6	0.16	95.99	−0.03
0.9988	1302.8	0.15	96.15	−0.02
		xCH$_3$[O(CH$_2$)$_3$]$_2$OH + (1 − x)C$_5$H$_{11}$OH		
0.0012	1274.2	0.04	82.55	−0.01
0.0027	1274.2	0.06	82.57	−0.01
0.0061	1274.2	0.29	82.62	−0.04
0.0077	1274.5	0.69	82.60	−0.09
0.0097	1274.7	1.02	82.61	−0.13
0.0145	1275.0	1.63	82.65	−0.21
0.0268	1275.5	2.87	82.77	−0.36
0.0418	1276.2	4.41	82.92	−0.46
0.0583	1276.7	5.76	83.11	−0.74
0.0740	1277.2	6.99	83.29	−0.89
0.0921	1277.8	8.35	83.51	−1.07
0.1290	1278.8	10.62	83.97	−1.37
0.1745	1279.7	12.61	84.60	−1.64
0.2223	1281.7	15.24	85.14	−1.99
0.2734	1283.4	17.08	85.78	−2.25
0.3037	1284.1	17.63	86.21	−2.33
0.3448	1285.4	18.45	86.75	−2.45
0.4043	1287.1	18.96	87.56	−2.54
0.4472	1288.4	19.07	88.14	−2.57
0.4965	1289.6	18.57	88.86	−2.51
0.5396	1290.4	17.63	89.52	−2.39
0.5750	1291.8	17.43	89.96	−2.37
0.6138	1293.1	16.81	90.48	−2.30
0.6562	1294.4	15.72	91.07	−2.17
0.7028	1295.6	14.29	91.75	−1.97
0.7454	1296.8	12.81	92.36	−1.78
0.7863	1297.9	11.19	92.96	−1.56
0.8273	1299.2	9.62	93.53	−1.34
0.8549	1300.0	8.41	93.92	−1.18
0.8839	1300.6	6.83	94.37	−0.96
0.9062	1301.2	5.71	94.70	−0.80
0.9244	1301.4	4.48	95.00	−0.36
0.9426	1301.7	3.33	95.29	−0.47
0.9618	1302.0	2.07	95.61	−0.29
0.9780	1302.3	1.04	95.87	−0.15
0.9894	1302.6	0.35	96.05	−0.05
0.9970	1302.6	0.25	96.18	−0.04
		xCH$_3$[O(CH$_2$)$_3$]$_2$OH + (1 − x)C$_7$H$_{15}$OH		
0.0011	1327.5	0.09	97.40	0.01
0.0031	1327.3	−0.09	97.42	0.02
0.0064	1327.1	0.03	97.42	0.01
0.0090	1327.0	0.18	97.43	−0.01
0.0130	1326.8	0.36	97.43	−0.04
0.0229	1326.4	0.90	97.43	−0.11
0.0348	1326.0	1.61	97.42	−0.19
0.0452	1325.4	1.96	97.45	−0.23
0.0596	1324.8	2.65	97.46	−0.32
0.0803	1323.8	3.43	97.48	−0.42
0.1014	1322.7	4.08	97.52	−0.49
0.1274	1321.3	4.74	97.57	−0.57
0.1612	1219.7	5.64	97.61	−0.69
0.1962	1218.2	6.55	97.64	−0.81
0.2351	1216.9	7.70	97.61	−0.96
0.2699	1216.0	8.81	97.56	−1.11
0.3029	1214.1	8.64	97.67	−1.08
0.3355	1312.7	8.79	97.70	−1.09
0.3737	1311.9	9.62	97.63	−1.20
0.4159	1311.4	10.69	97.49	−1.36
0.4763	1310.1	11.19	97.39	−1.43
0.5322	1308.6	10.92	97.34	−1.39
0.5839	1307.6	10.69	97.25	−1.37
0.6402	1307.0	10.54	97.08	−1.36
0.6819	1306.0	9.61	97.04	−1.23
0.7168	1305.5	8.99	96.96	−1.16
0.7706	1305.2	5.21	96.77	−1.03
0.8238	1305.0	7.18	96.58	−0.94
0.8775	1304.9	5.88	96.38	−0.77
0.9193	1304.4	4.16	96.29	−0.54
0.9336	1304.8	4.14	96.17	−0.55
0.9484	1305.0	3.85	96.08	−0.52
0.9696	1304.1	2.19	96.13	−0.29
0.9857	1303.6	1.07	96.14	−0.14
0.9942	1303.2	0.34	96.17	−0.04

The excess quantities were calculated from :

$$K_{s,m}^{E} = K_{s,m} - K_{s,m}^{id}, \tag{3}$$

where $K_{s,m}^{id}$ [20,21] is

$$K_{s,m}^{id} = \sum x_i \left[K_{s,i}^{*} - T \cdot A_{p,i}^{*} \left\{ \left(\Sigma x_i \cdot A_{p,i}^{*} / \Sigma x_i \; C_{p,i}^{*} \right) - \left(A_{p,i}^{*} / C_{p,i}^{*} \right) \right\} \right]. \tag{4}$$

where, $A_{p,i}^{*}$ is product of the molar volume and the isobaric expansivity, $C_{p,i}^{*}$ is the isobaric molar heat capacity, and $K_{s,i}^{*}$ is the product of the molar volume V_i^{*} and the isentropic compressibility $\kappa_{s,i}^{*}$. The ρ of the mixture at the appropriate mole fractions used in the ultrasonic speed measurements, were obtained from molar volumes of pure components and excess molar volumes from the cubic-spline interpolation reported in Ref. [1].

The deviations of the ultrasonic speeds from their values in an ideal mixture were calculated from [4,21] :

$$u^{D} = u - u^{id}, \tag{5}$$

where $u^{id} = V_m^{id} / \left(M \cdot K_{s,m}^{id} \right)^{1/2}$, (6)

Also, the mixing function δu is defined by

$$\delta u = u - \sum x_i u_i^{*}, \tag{7}$$

The values of $K_{s,m}^{E}$, u^{D}, and δu were fitted for each mixture by an equation of the type :

$$F(x) = x(1-x) \sum_{i=0}^{n} a_i (2x-1)^i. \tag{8}$$

Values of coefficients a_i, calculated by the method of least squares with all points weighted equally, and their standard deviations σ are summarized in Table 3. Experimental results for $K_{s,m}^{E}$, and u^{D} are plotted against x in Figures 1 and 2.

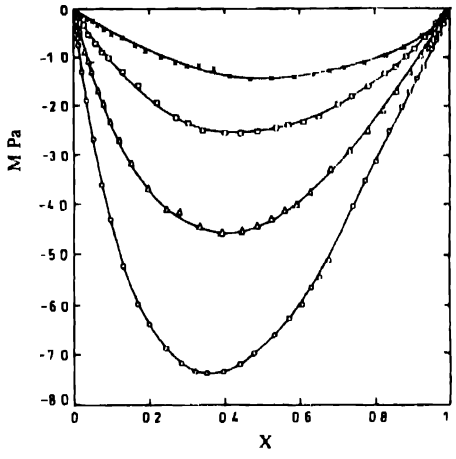

Figure 1. Values of $K_{s,m}^{E}$ at 298.15 K for $x CH_3[O(CH_2)_3]_2OH + (1-x)$ $C_nH_{2n+1}OH$, methanol (o), 1-propanol (Δ), 1-pentanol (□); 1-heptanol (×

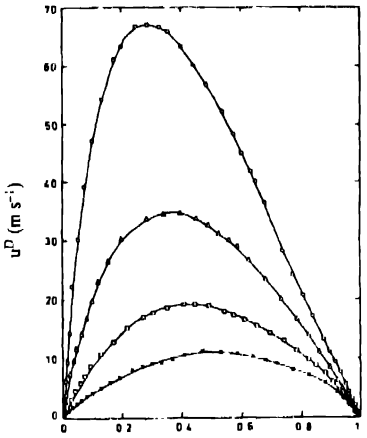

Figure 2. Values of u^{D} of the speeds of sound from their ideal values at 298 15 K for $x CH_3[O(CH_2)_3]_2OH + (1-x)C_nH_{2n+1}OH$, methanol (o), 1-propanol (Δ); 1-pentanol (□), 1-heptanol (×)

Table 3. Parameters of eq (8) and standard deviations σ

$F(x)$	a_0	a_1	a_2	a_3	a_4	σ
			$x CH_3[O(CH_2)_3]_2OH + (1-x)CH_3OH$			
δu/(m s^{-1})	301 64	−171 10	66.25	−78.72	69 56	0 41
u^{D}/(m s^{-1})	221 82	−177 65	88 96	−119 74	103 05	0.44
$K_{s,m}^{E}$/(mm^3 mol^{-1} MPa^{-1})	−27 64	13.62	−3.43	8 59	−8 57	0 04
			$x CH_3[O(CH_2)_3]_2OH + (1-x)C_3H_7OH$			
δu/(m s^{-1})	84 39	−31 15	21.14	−17 96		0 35
u^{D}/(m s^{-1})	128 42	−66 69	41 90	−27.79		0.36
$K_{s,m}^{E}$/(mm^3 mol^{-1} MPa^{-1})	−17 54	6 44	−3.61	2.79		0.04
			$x CH_3[O(CH_2)_3]_2OH + (1-x)C_5H_{11}OH$			
δu/(m s^{-1})	4 86	1 02	9 40	−8 63		0 23
u^{D}/(m s^{-1})	74 21	−17.87	11.55	−3 98		0.23
$K_{s,m}^{E}$/(mm^3 mol^{-1} MPa^{-1})	−10 04	1.87	−1.30	0 42		0.03
			$x CH_3[O(CH_2)_3]_2OH + (1-x)C_7H_{15}OH$			
δu/(m s^{-1})	−24 66	7 73	−3.35	3.42	15.40	0 26
u^{D}/(m s^{-1})	44.11	1 44	−9.79	12.04	32 65	0.30
$K_{s,m}^{E}$/(mm^3 mol^{-1} MPa^{-1})	−5 59	−0,37	−1.20	−1 77	−4.14	0.04

We have attempted to explain the physico-chemical behaviour of the mixtures in order to explore the strength and nature of the interactions between the components by deriving various thermodynamic parameters from the ultrasonic speed and density data. Various parameters such as intermolecular free length L_f [23], van der Waal's constant b, molecular radius r [23], geometrical volume B, molar surface area Y, available volume V_a [22], molar sound velocity R [24], collision factor S [25], specific acoustic impedance Z [26], relative association R_A [27], and molecular association M_A [28] have been calculated using the following relations :

$$L_f = K/(u \cdot \rho^{1/2}), \tag{9}$$

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

$$r = (3b/16\pi N)^{1/3}, \tag{11}$$

$$B = (4/3)\pi r^3 N, \tag{12}$$

$$Y = (36\pi N B^2)^{1/3}, \tag{13}$$

$$V_a = V(1 - u/u_\infty), \tag{14}$$

$$V_0 = V - V_a, \tag{15}$$

$$R = M \cdot u^{1/3}/\rho, \tag{16}$$

$$S = uV/u_\infty B, \tag{17}$$

$$Z = u\rho, \tag{18}$$

$$R_A = (\rho_{mix}/\rho)(u/u_{mix})^{1/3}, \tag{19}$$

$$M_A = \left[\left(u_{mix}/\Sigma x_i u_i\right)^2 - 1\right], \tag{20}$$

where L_f is the free length of ideal mixing, K is a temperature dependent constant (= (93.875 + 0.375T) × 10^{-8}) [22], V_0 is the volume at absolute zero, u_∞ is taken as 1600 m s^{-1}. These parameters are listed in Table 4 for the pure components. The variation of V_a, L_f, R_A, Z, R, and M_A for mixtures with mole fraction of x are graphically shown in Figures 3 and 4.

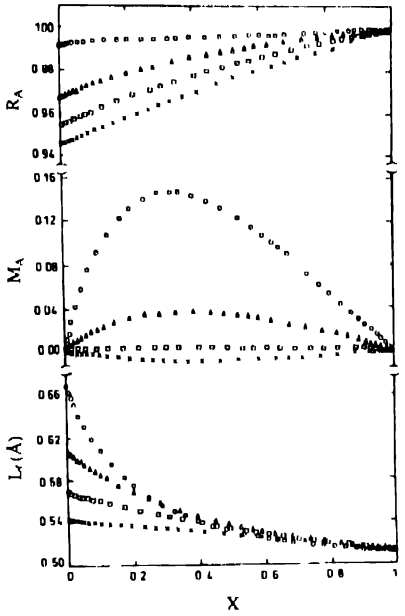

Figure 3. L_f, R_A and M_A for $xCH_3[O(CH_2)_3]_2OH$ + $(1 \cdot x)C_nH_{2n+1}OH$, methanol (o), 1-propanol (Δ), 1-pentanol (□), 1-heptanol (×).

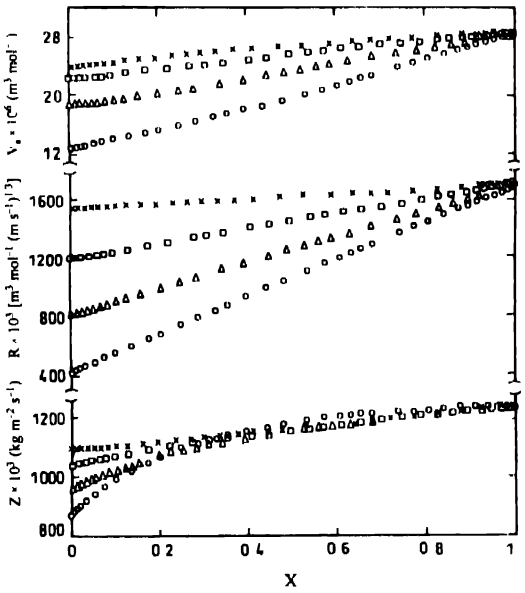

Figure 4. Z, R and V_a for $xCH_3[O(CH_2)_3]_2OH$ + $(1-x)C_nH_{2n+1}OH$, methanol (o), 1-propanol (Δ), 1-pentanol (□), 1-heptanol (×)

Table 4. Values of the derived parameters of the pure components at 298 15 K

Component	$b \times 10^6$ m^3	r nm	$B \times 10^6$ m^3 mol^{-1}	S	$R \times 10^3$ m^3 mol^{-1} (m s^{-1})$^{1/3}$	$V_a \times 10^6$ m^3 mol^{-1}	L_f Å	$V_0 \times 10^6$ m^3 mol^{-1}	Y Å	$Z \times 10^{-3}$ kg m^{-2} s^{-1}
Dipropylene glycol monomethyl ether	148 05	0 245	37 08	3 42	1699	28 86	0 512	126 69	45 31	1241
Methanol	36 86	0 154	9.21	3 04	421	12 71	0.667	28 03	17.91	865
1-Propanol	69 69	0 191	17 57	3 22	800	18.58	0 605	56.59	27 54	962
1-Pentanol	102.09	0.216	25.41	3 41	1178	22.15	0 568	86.53	35 22	1033
1-Heptanol	133.20	0.236	33.15	3.52	1545	23 93	0 542	116.69	42 05	1087

It is observed from Figures 3–6 and Table 2 that u, R_A, Z, R, and V_a increase with mole fraction of x, while $K_{s,m}$ and

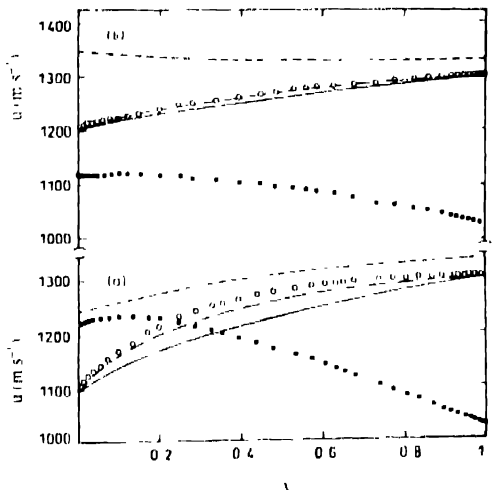

Figure 5. Experimental and calculated ultrasonic speeds u, ooo, u_{CFT} —, u_J ----, u_N – – –, u_{FLT} ●●● for xCH$_3$[O(CH$_2$)$_3$]$_2$OH + (1 − x)C$_n$H$_{2n+1}$OH (a) methanol and (b) 1-propanol

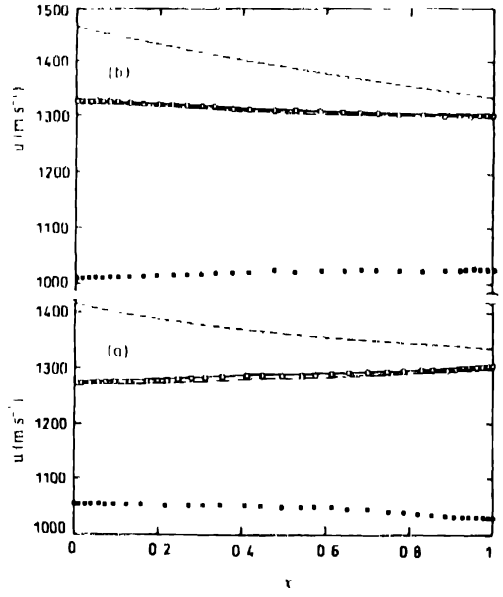

Figure 6. Experimental and calculated ultrasonic speeds u, ooo, u_{CFT} —, u_J ----, u_N – – –, u_{FLT} ●●● for xCH$_3$[O(CH$_2$)$_3$]$_2$OH + (1 − x)C$_n$H$_{2n+1}$OH, (a) 1-pentanol and (b) 1-heptanol

L_f decrease. The decrease in $K_{s,m}$ and L_f with x in the present investigations, indicates significant interaction between dipropylene glycol monomethyl ether and methanol molecules. The addition of dipropylene glycol monomethyl ether to alkanol tends to cause breaking of self-associated alkanol molecules with a consequent increase in u and L_f. However, because of simultaneous formation of strong hydrogen bonds between the unlike molecules, there is a compensating effect resulting in an overall decrease in $K_{s,m}$ and L_f or increase in u with x.

In the present investigation, relative association R_1 is found to increase with mole fraction of dipropylene glycol monomethyl ether (Figure 3) for all the mixtures. Relatively higher values of R_A for dipropylene glycol monomethyl ether–methanol systems, signifies that unlike interactions are relatively strong compared to like interactions; the former tends to increase while the latter causes a decrease in R_1. Similarly, Figure 3 shows the large deviations in M_1 for dipropylene glycol monomethyl ether + methanol system and these deviations decrease with increase in the chain length of the alkanol. Thus, it concluded that the non-ideality of the systems varies in the order methanol > 1-propanol > 1-pentanol > 1-heptanol. A sharp increase in Z and R with x (Figure 4) suggests strong interaction between the dipropylene glycol monomethyl ether and methanol molecules.

For all the mixtures studied, $K_{s,m}^{L}$ is negative over the whole mole fraction range and shows a minimum in the sequence: methanol > 1-propanol > 1-pentanol > 1-heptanol, while in the same sequence, the minimum is shifted to lower values of x. This behaviour may be compared with the $K_{s,m}$ results for diethylene glycol monomethyl [29] ether the magnitude of $K_{s,m}$ decreases from methanol to 1-propanol with the replacement of ethyl by propyl groups at the middle of diethylene glycol monomethyl ether and then the trend is reverse. The overall behaviour of $K_{s,m}^{L}$ is similar to that of u^D but with an opposite variation with the number of carbon atoms in the alcohol molecule. However, the behaviour of $K_{s,m}^{L}$ is inconsistent with V_m^L for 1-pentanol and 1-heptanol [1]. Also, the behaviour of excess molar volume seems to be consistent with a minimum value of $K_{s,m}^{L}$ and a maximum value for u^D with methanol and 1-propanol. This is normal because u is generally higher when the structure has high rigidity. Negative values of $K_{s,m}^{L}$ mean that the structure is less compressible than the corresponding ideal mixture, suggesting that there may be strong intermolecular hydrogen bonding with methanol and 1-propanol. As the ether is added to alcohol, thereby causing a breakdown of self-associated ether, or both and hence contribute to a denser packing of the molecules through hydrogen bonding, the speed of sound increases and $K_{s,m}^{L}$ decreases. However, V_m^L is positive for 1-pentanol and 1-heptanol, although $K_{s,m}^{L}$ is negative and u^D is likewise positive from methanol to 1-heptanol, indicating that when the mixture is created "excess free volumes" decreases and is higher in mixtures containing dipropylene glycol monomethyl ether with methanol. The effect is that with increasing the n-alkyl chain end length, interstitial accommodation become less important, and the molecules of the two components cannot be easily accommodated

This additional rigidity is a good reason for the positive values of u^{D}. As suggested earlier, the volume behaviour of dipropylene glycol monomethyl ether + n-alcohol is the result of several opposing effects; the present results for $K_{S,m}^{I}$ and u^{D} support this suggestion. Finally, from Figure 7, a similar but opposite variation of $K_{S,m}^{I}$ and u^{D} with the n-alkyl chain end length of alcohol has been found, whilst δu decreases regularly with n. Again, it is interesting to note that both δu and u^{D} can be correlated well with the $K_{S,m}^{I}$.

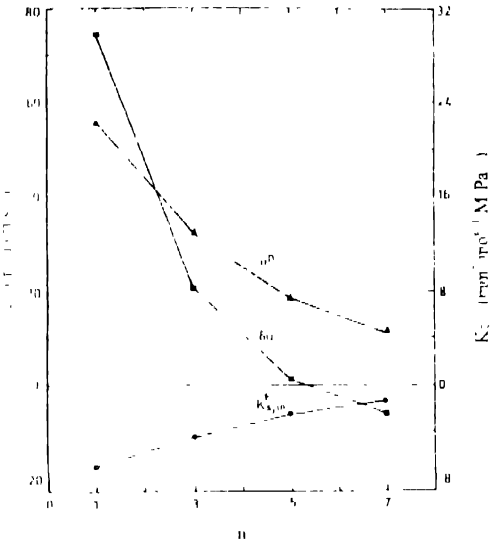

Figure 7. Plots of $K_{S,m}^{I}$ ● u^{D}, ▲, δu ■ at 298.15 K against n for $x\mathrm{CH_3[OCH(CH_3)CH_2]_2OH} + (1-x)\mathrm{C_nH_{2n+1}OH}$.

For comparison, we have calculated the theoretical values of ultrasonic speeds from the following empirical equations :

Collision Factor Theory [23] :

$$u_{\mathrm{CFT}} = u_{\infty}\left\{xS_1 + (1-x)S_2\right\}\left[\left\{xB_1 + (1-x)B_2\right\}/V\right], \quad (21)$$

Free length theory [22] :

$$u_{\mathrm{FLT}} = K/\left(L_f \rho^{1/2}\right), \quad (22)$$

Junjie equation [30] :

$$u_{\mathrm{J}} = \left\{\left(xM_1/\rho_1\right) + \left(1-x\right)M_2/\rho_2\right\}/ \left[\left\{xM_1 + (1-x)M_2\right\}^{1/2} \times \left\{\left(xM_1/\rho_1 u_1^2\right) + \left(1-x\right)M_2/\rho_2 u_2^2\right\}^{1/2}\right], \quad (23)$$

Nomoto equation [31] :

$$u_{\mathrm{N}} = \left[\left\{xR_1 + (1-x)R_2\right\}/\left\{xV_1 + (1-x)V_2\right\}\right]^3. \quad (24)$$

The computed u_{CFT}, u_{FLT}, u_{J} and u_{N} values are shown in Figures 5 and 6 for comparison with experimental values for all the mixtures. The results clearly indicate that the simple Nomoto expression and collision factor theory predict the experimental data extremely well for all the mixtures except with 1-propanol whereas the Junjie expression shows the maximum deviation and the free length theory gives the greatest deviations for all the present binary mixtures.

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