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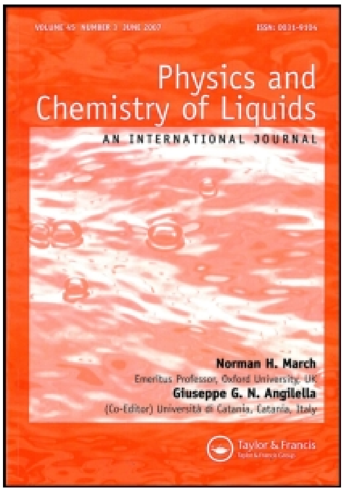

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SPEEDS OF SOUND AND ISENTROPIC COMPRESSIBILITIES OF ALKYL CELLOSOLVE WITH ALIPHATIC ALCOHOLS AT 308.15K

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Speeds of sound are measured in binary mixtures of alkyl cellosolve (2-ethoxyethanol and 2-butoxyethanol) with aliphatic alcohols at 308.15K. Aliphatic alcohols includes methanol, propan-1-ol, butan-1-ol, 2 methyl propan-1-ol, 2-methyl propan-2-ol and pentan-1-ol. Experimental sound speed data are used along with the density values to compute isentropic compressibilities in these mixtures. Deviations in isentropic compressibilities are negative in all the systems except in mixtures containing pentan-1-ol as non-common component, where as an inversion in sign of the function is observed. Further, speeds of sound are evaluated on the basis of Jacobson's free length theory and Schaff's collision factor theroy. The predicted values are in good agreement with the experimental results.

Keywords: Speeds of sound, 2-ethoxyethanol, 2-butoxyethanol, aliphatic alcohols.

1. INTRODUCTION

It is well known that ultrasound techniques have wide range of applications such as in industry, in medical scanning, in equipment testing etc. Molecular association in solution and correlation of sound speed with various parameters such as isentropic compressibilities, free volume etc. can be very well studied by measurement of speed of sound in liquid mixtures. Ultrasonic speed and its related thermodynamic properties have been extensively used [1–10] to study physicochemical behaviour and molecular interactions in a variety of binary liquid mixtures. However no systematic effort has been made to study the interaction between alkyl cellosolve with aliphatic alcohols. We report here new experimental data on speed of sound and isentropic compressibility of alkyl cellosolves with methanol, propan-1-ol, butan-1-ol, 2 methyl propan-1-ol, 2 methyl propan-2-ol and pentan-1-ol at 308.15 K. The aim of this programme is to characterise the moelcular interactions between aliphatic alcohol and alkyl cellosolve in terms of deviation in isentropic compressibility. Further, the data included in the paper throw light on the variation of deviation in compressibility with chain length and branching of alcohols.

2. EXPERIMENTAL

The liquids were purified as described earlier [11, 12] The purity of the samples was checked by comparing the measured densities of the components with those reported in the literature [13, 14]. Speed of sound was measured with a single-crystal interferometer at a frequency of 2MHZ and the data were accurate to within ±0.15%. All measurements were made at constant temperature employing a thermostat that could be maintained to ±0.01K.

3. RESULTS AND DISCUSSION

Isentropic compressibilities (k_s) were computed from the density (ρ) and sound speed (u) data, using the equation

$$k_s = \frac{1}{u^2 \rho} \tag{1}$$

Density of pure components are measured using a bicapillary pycnometer and in case of mixtures densities were computed from measured excess volume data, from the relation

$$\rho = \frac{x_1 M_1 + x_2 M_2}{V_m} \tag{2}$$

and

$$Vm = X_1 V_1 + X_2 V_2 + V^E$$

where x_1 and x_2 are the mole fractions, M_1 and M_2 are molecular weights and V_1 and V_2 are molar volumes of alkyl cellosolve (1) and alcohols (2) respectively. Deviations in isentropic compressibility (Δk_s) are evaluated from the equation

$$\Delta k_s = k_s - (\phi_1 k_{s1} + \phi_2 k_{s2}) \tag{3}$$

where ϕ_1 and ϕ_2 are the volume fractions of components 1 and 2 respectively and k_s, k_{s1}, and $k_{s,2}$ are the isentropic compressibilities of the mixture and components 1 and 2 respectively. Data on sound speed, density, isentropic compressibility and deviations in compressibility (Δk_s) are given in Table II as a function of volume fraction (ϕ), variation of the Δk_s with ϕ are shown in Figures 1 and 2. Values of Δk_s are negative in all the systems except mixtures continuing pentan-1-ol as a non-common component. Negative values of Δk_s indicate

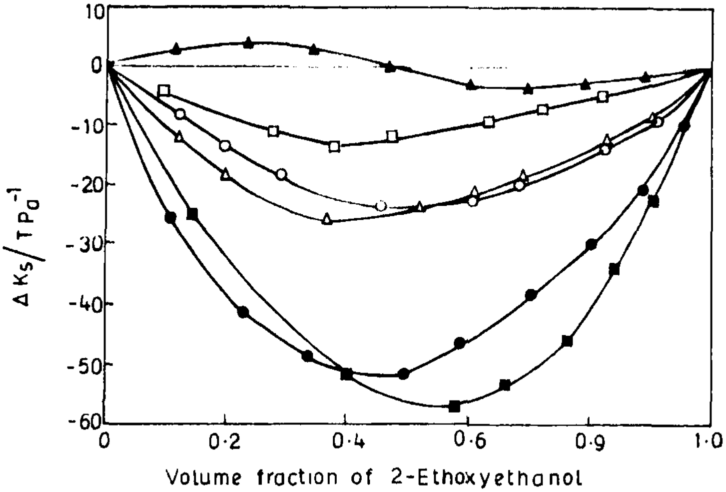

FIGURE 1 Deviations in Isentropic compressibilities (Δk_S) for 2-Ethoxyethanol + Methanol (■), + 1-Propanol (Δ), + 1-Butanol (□), + 2-Methyl 1-Propanol (0), + 2-Methyl 2-Propanol (●) and + 1-Pentanol (▲) at 308.15 K

that the interaction between unlike molecules is stronger than between like molecules.

Further the interaction decreases with increase in chain length of both alkoxy alcohols and aliphatic alcohols. The inter molecular free length, L_f of pure liquid has been evaluated by the thermodynamic method using the Eyring and Hirschfelder [15] relation:

$$L_f = 2v_a/y \tag{4}$$

where

$$v_a = v_t - v_o$$

and

$$v_o = v_t\left(1 - \frac{t}{t_c}\right)0.3$$

in which Va, V_T and V_0 are the available volume, molar volume at

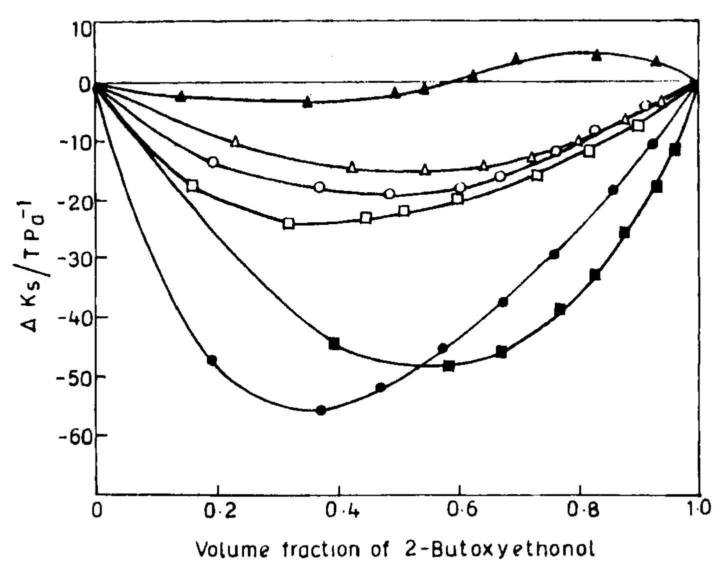

FIGURE 2 Deviations in Isentropic compressibilities (Δk_S) for 2-Ethoxyethanol + Methanol (■), + 1-Propanol (Δ), + 1-Butanol (□), + 2-Methyl 1-Propanol (0), + 2-Methyl 2-Propanol (●) and + 1-Pentanol (▲) at 308.15 K

temperature T and absolute zero temperature, respectively. T_C and Y are the critical temperature and total surface area per mole. This concept of free length has been extended to the mixtures [16] and expressed as

$$L_f \,\mathrm{mix} = \frac{2(V_m - (x_1 V_{01} + x_2 V_{02}))}{x_1 Y_1 + x_2 Y_2} \tag{5}$$

The ultrasonic speed in the mixture can be evaluated by the free length theory of Jacobson's formula [17, 18]

$$U_{\mathrm{mix}} = \frac{K}{L_{\mathrm{mix}}^{1/2} \rho_{\mathrm{mix}}} \tag{6}$$

where K is a constant which is temperature dependent [18] but independent of the nature of the liquid. ρ_{mix} is the density of the mixture.

Schaffs [19], on the basis of the collision factor theory developed the following relation for the ultrasonic speed in pure liquids.

$$U = U_\infty S r_j = U_\infty S \frac{B}{V_m} \tag{7}$$

where u_∞ is 1600 m·s^{-1} by Schaffs [20] S is the collision factor and $r_j = B/V_m$ is space filling factor, B is actual volume of the molecule per mole and V_m = molar volume. The actual volume B of the molecule for pure components is given by the relation

$$B = \frac{4}{3} r_m^3 N \tag{8}$$

where r_m is the molecular diameter and N is avagadro number. The molecular diameter was calculated using the relation [21].

$$d^{5/2} = \frac{1}{7.21 \times 10^{19}} \times \frac{V \cdot \sigma^{1/4}}{T_C^{1/4}} \tag{9}$$

where T_C is critical temperature, σ is surface tension which is related to density ρ and sound velocity u by the relation

$$\sigma = \{u(6.3 \times 10^{-4}\rho)\}^{3/2} \tag{10}$$

The above concept of Schaffs [22, 19] for pure components was extended to binary liquid mixtures by Nutsch-Kuhnkies [16] who obtained the relation

$$u_{\text{mix}} = u_{\infty}[x_1 s_1 + x_2 s_2]\frac{(x_1 B_1 + x_2 B_2)}{V_m} \tag{11}$$

The surface area γ and collission factor S of the pure components used in FLT and CFT were calculated using the experimental sound velocities and densities. Critical temperature, surface tension which were used in the calculation of molar volume at absolute zero V_0 and the average molecular radius r_m were taken from the literature [14, 23–25]. The values of molar volume V, available volume Va, free length L_f, surface area, collission factor, and the average radius of the molecules of the pure components are given in Table I. Sound speed data predicted in terms of FLT and CFT are included in Table II along with experimental results.

The values of Δk_s are fitted to an empirical equation of the form,

$$\Delta k_s = x_1 x_2[b_0 + b_1(x_1 - x_2) + b_2(x_1 - x_2)^2] \tag{12}$$

where b_0, b_1 and b_2 are empirical parameters. The values of the parameters, evaluated from least square method, are included in Table III along with standard deviation, $\sigma(\Delta k_s)$. Values of $\sigma(\Delta k_s)$ are obtained using the equation,

$$\sigma(\Delta k_s) = \left[\frac{\Sigma(\Delta k_{s(\text{cal})} - \Delta k_{s(\text{expth})})}{n - p}\right]^{1/2}$$

where n is the number of experimental data and p is the number of parameters.

TABLE I Molar volume V, Molar volume at absolute zero V_0, available volume V_a, free length, L_f, and surface area, Y, collision factor S and average molecular radius, r_m, of the pure liquiid components at 308.15K.

Component	V	V_0	V_a	L_f	Y	S	r_m A°
	$Cm^3:mol^{-1}$			A°			
Ethyl cellosolve	98.176	77.867	20.309	0.525	77.41	1.685	2.634
Butyl cellosolve	132.973	109.334	23.639	0.526	89.85	1.705	2.916
Methanol	41.200	31.271	9.929	0.669	29.69	1.784	1.835
Propan-1-ol	75.822	58.717	17.105	0.604	56.65	1.727	2.344
Butan-1-ol	92.788	73.152	19.636	0.588	66.78	1.688	2.546
2 methyl propan-1-ol	93.715	73.130	20.585	0.613	67.19	1.643	2.538
2 methyl propan-2-ol	96.190	72.588	23.602	0.670	70.51	1.555	2.551
Pentan-1-ol	109.586	87.714	21.872	0.571	76.68	1.684	2.717

TABLE II Volume fraction (ϕ_1) of Ethyl Cellosolve and Butyl Cellosolve density ρ, sound velocity u, FLT, (u), CFT, (u) isentropic compressibility (from equation 2) and deviation in isentropic compressibility Δk_s (from equation 3) with alcohols at 308.15K respectively.

ϕ_1	ρ $g.cm^{-3}$	u ms^{-1}	$FLT(u)$ ms^{-1}	$CFT(u)$ ms^{-1}	$k_s\,Tpa^{-1}$	$\Delta k_S\,Tpa^{-1}$
		Ethyl Cellosolve (1) + Methanol (2)				
0.0000	0.77771	1079	–	–	1104	–
0.1451	0.79902	1109	1102	1113	1018	−25
0.4045	0.83710	1164	1145	1170	881	−51
0.5698	0.86246	1200	1174	1204	805	−57
0.6583	0.87535	1268	1191	1220	770	−55
0.7617	0.88974	1237	1212	1237	734	−46
0.8421	0.90002	1248	1229	1249	713	−34
0.9029	0.90754	1256	1243	1257	698	−22
0.9534	0.91369	1264	1256	1263	685	−20
1.0000	0.91797	1266	–	–	680	–
		Ethyl Cellosolve (1) + propan-1-ol (2)				
0.0000	0.79265	1184	–	–	900	–
0.1199	0.80781	1199	1193	1195	861	−12
0.1998	0.81788	1208	1198	1202	838	−18
0.3622	0.82940	1225	1205	1210	795	−25
0.5148	0.85742	1236	1223	1229	763	−23
0.6059	0.86883	1244	1231	1236	745	−21
0.6816	0.87833	1247	1237	1242	732	−18
0.8280	0.89664	1258	1250	1254	705	−13
0.8893	0.90429	1261	1256	1258	695	−9
1.0000	0.91797	1266	–	–	680	–

TABLE II Continued

Ethyl Cellosolve (1) + butan-1-ol (2)						
0.0000	0.79885	1211	–	–	854	–
0.0982	0.81034	1217	1216	1216	833	−4
0.2747	0.83105	1229	1226	1226	797	−10
0.3783	0.84330	1237	1232	1232	775	−13
0.4649	0.85359	1240	1236	1237	762	−11
0.6284	0.87308	1248	1246	1246	735	−9
0.7195	0.88403	1252	1250	1251	722	−7
0.8153	0.89557	1257	1256	1255	707	−5
0.8757	0.90287	1260	1259	1259	699	−3
1.0000	0.91797	1266	–	–	680	–
Ethyl Cellosolve (1) + 2 Methyl propan-1-ol						
0.0000	0.79095	1168	–	–	927	–
0.1249	0.80650	1182	1180	1180	887	−8
0.1942	0.81517	1191	1186	1187	865	−14
0.2958	0.82795	1202	1196	1197	836	−18
0.4538	0.84793	1221	1211	1212	791	−24
0.6151	0.86843	1237	1227	1228	753	−22
0.6859	0.87747	1242	1234	1235	738	−19
0.8267	0.89552	1254	1248	1249	710	−12
0.9107	0.90638	1262	1257	1257	693	−9
1.0000	0.91797	1266	–	–	680	–
Ethyl Cellosolve (1) + 2 Methyl propan-2-ol						
0.0000	0.77060	1083	–	–	1106	–
0.1112	0.78681	1109	1100	1102	1033	−26
0.2283	0.80386	1134	1119	1123	967	−42
0.3429	0.82057	1156	1138	1144	912	−48
0.4957	0.84293	1186	1165	1171	843	−52
0.5877	0.85644	1200	1182	1188	810	−46
0.7094	0.87443	1222	1205	1211	766	−38
0.8012	0.88808	1238	1224	1228	735	−30
0.8928	0.90179	1254	1243	1246	705	−21
1.0000	0.91797	1266	—	—	680	–
Ethyl Cellosolve (1) + pentan-1-ol (2)						
0.0000	0.80440	1244	–	–	803	–
0.1115	0.81618	1244	1247	1246	792	3
0.2313	0.82900	1245	1251	1249	778	4
0.3395	0.84092	1247	1254	1251	764	3
0.4712	0.85572	1251	1257	1254	746	1
0.6081	0.87140	1257	1259	1257	726	−2
0.6989	0.88196	1260	1261	1259	714	−3
0.7894	0.89262	1262	1263	1261	703	−3
0.8904	0.90468	1265	1264	1264	691	−2
1.0000	0.91797	1266	–	–	680	–

TABLE II Continuded

Butyl Cellosolve (1) + Methanol (2)						
0.0000	0.77771	1079	–	–	1104	–
0.3968	0.82500	1165	1140	1175	893	– 44
0.5882	0.84702	1208	1178	1217	809	– 48
0.6728	0.85641	1227	1196	1235	775	– 46
0.7642	0.86619	1246	1218	1252	744	– 39
0.8285	0.87277	1259	1234	1263	723	– 33
0.8796	0.87802	1268	1249	1271	708	– 26
0.9261	0.88216	1275	1261	1276	697	– 18
0.9597	0.88521	1280	1271	1280	689	– 12
1.0000	0.88873	1283	–	–	684	–
Butyl Cellosolve (1) + propan-1-ol (2)						
0.0000	0.79265	1184	–	–	900	–
0.2352	0.81610	1206	1200	1209	842	– 10
0.4297	0.83501	1232	1217	1229	789	– 14
0.5402	0.84562	1241	1228	1240	768	– 15
0.6394	0.85509	1250	1238	1250	748	– 14
0.7214	0.86289	1259	1247	1258	731	– 13
0.8010	0.87043	1266	1257	1265	717	– 10
0.8824	0.87805	1273	1267	1273	702	– 7
0.9355	0.88295	1278	1274	1277	693	– 4
1.0000	0.88873	1283	–	–	684	–
Butyl Cellosolve (1) + butan-1-ol (2)						
0.0000	0.79885	1211	–	–	854	–
0.1666	0.81393	1234	1220	1222	807	– 18
0.3171	0.82762	1248	1229	1233	776	– 24
0.4482	0.83936	1256	1238	1242	755	– 23
0.5098	0.84490	1260	1242	1246	745	– 22
0.5906	0.85217	1265	1248	1252	733	– 20
0.7288	0.86454	1273	1259	1263	714	– 16
0.8177	0.87195	1276	1266	1269	704	– 12
0.8930	0.87920	1280	1273	1275	694	– 8
1.0000	0.88873	1283	–	–	684	–
Butyl Cellosolve (1) + 2 methyl propan-1-ol						
0.0000	0.79095	1168	–	–	927	–
0.1945	0.81012	1194	1185	1188	866	– 14
0.3728	0.82783	1215	1203	1207	818	– 18
0.4878	0.83890	1229	1215	1220	789	– 19
0.6044	0.84833	1244	1227	1231	762	– 18
0.6732	0.85701	1250	1237	1241	747	– 16
0.7612	0.86557	1258	1249	1252	730	– 12
0.8272	0.87198	1264	1258	1260	718	– 8
0.9145	0.88045	1274	1270	1272	700	– 5
1.0000	0.88873	1283	–	–	684	–

TABLE II Continuded

Butyl Cellosolve (1) + 2 Methyl propan-2-ol						
0.0000	0.77060	1083	–	–	1106	–
0.1934	0.79420	1135	1110	1116	977	– 47
0.3685	0.81504	1171	1138	1147	895	– 56
0.4710	0.82708	1189	1157	1167	855	– 52
0.5767	0.83942	1207	1178	1188	818	– 45
0.6655	0.84976	1222	1197	1206	788	– 37
0.7602	0.86041	1240	1219	1226	755	– 30
0.8551	0.87188	1257	1243	1248	726	– 19
0.9231	0.87981	1269	1261	1264	706	– 10
1.0000	0.88873	1283	–	–	684	–
Butyl Cellosolve (1) + pentan-1-ol (2)						
0.0000	0.80440	1244	–	–	803	–
0.1477	0.81680	1250	1248	1249	783	– 2
0.3558	0.83428	1258	1255	1257	757	– 3
0.4994	0.84637	1262	1261	1263	742	– 2
0.5485	0.85051	1263	1262	1265	737	– 1
0.6266	0.85710	1264	1266	1268	730	1
0.7030	0.86355	1266	1269	1271	722	3
0.8322	0.87448	1271	1275	1276	708	4
0.9288	0.88268	1276	1280	1280	696	3
1.0000	0.88873	1283	–	–	684	–

TABLE III Values of the parameters, b_0, b_1 and b_2 of equation (13) and the standard deviation, σ (Δk_s) at 308.15K.

System	b_0	b_1	b_2	$\sigma(\Delta k_s)$
Ethyl cellosolve + Methanol	– 232.67	– 34.25	24.01	2.0
Ethyl cellosolve + propan-1-01	– 93.03	15.51	– 14.55	1.3
Ethyl cellosolve + butan-1-01	– 93.08	17.43	– 10.94	0.8
Ethyl cellosolve + 2methyl propan-1-01	– 90.38	– 11.18	1.67	1.5
Metyl cellosolve + 2methyl propan-2-01	– 196.38	37.09	– 68.15	1.8
Ethyl cellosolve + pentan-1-01	0.35	– 34.82	7.43	0.4
Butyl cellosolve + Methanol	– 184.75	– 4.45	– 118.52	1.7
Butyl cellosolve + propan-1-01	– 59.94	– 7.93	– 1.46	0.3
Butyl cellosolve + butan-1-01	– 89.24	37.84	– 37.05	0.4
Butyl cellosolve + 2 methyl propan-0-01	– 78.65	16.38	10.78	0.9
Butyl cellosolve + 2 methyl propan-2-01	– 202.20	121.20	– 65.27	0.9
Butyl cellosolve + pentan-1-01	– 6.67	34.42	30.49	0.3

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