Speeds of Sound, Isentropic Compressibilities, and Excess Molar Volumes of an Alkanol + Cycloalkane at 303.15 K. 1. Results for Alkan-1-ols + Cyclohexane†

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Isentropic compressibilities K_S, excess isentropic compressibilities K_S^E, and excess molar volumes V^E have been determined from measurements of speeds of sound u and densities ρ of 10 binary mixtures of ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol, heptan-1-ol, octan-1-ol, nonan-1-ol, decan-1-ol, and dodecan-1-ol with cyclohexane at 303.15 K over the whole mole fraction range. The values of K_S^E decrease with number of carbon atoms of the alkanol going from positive values for ethanol + cyclohexane to negative for dodecan-1-ol + cyclohexane. The change of sign for K_S^E occurs between hexan-1-ol and heptan-1-ol. The trend of decreasing K_S^E with the chain length of alkanol is similar to that observed in case of V^E. However, the V^E values for all 10 mixtures of alkanol with cyclohexane are positive.

Introduction

The thermodynamic behavior of alkanols in nonpolar solvents shows pronounced nonideality, which along with spectral (IR and NMR) and dielectric behavior can at best be interpreted in terms of formation of hydrogen bonds, i.e., “associations” both in the pure liquid alkanols and in solution (Stokes and Marsh, 1976; Costas and Patterson, 1985). The extent of nonideality is strongly solvent-dependent (Costas and Patterson, 1985).

The speed of sound u, isentropic compressibility K_S, and excess molar volumes V^E are the properties sensitive to different kinds of association in the pure components and in the mixtures, and often they are related to local order. They have been used to investigate the molecular packing, molecular motion, and various types of intermolecular interactions and their strength, influenced by the size, shape, and chemical nature of component molecules.

There are few measurements on u and K_S for mixtures of alkanols with alicyclic hydrocarbons. The alicyclic hydrocarbons differ from alkanes. Cyclohexane is a rigid, globular, and very good order breaker (Bhattacharyya and Patterson, 1980), while alkanes are flexible, open-chain molecules whose orientation order increases with the increase of the chain length of alkyl group. Furthermore, there is a tendency of interstitial accommodation of hexane or heptane molecules into multimer alkanol species leading to negative V^E.

Systematic studies of speeds of sound, isentropic compressibilities, and excess molar volumes for binary mixtures of an alkanol with cycloalkanes have been undertaken. In this paper, we report studies on 10 binary mixtures of ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol, heptan-1-ol, octan-1-ol, nonan-1-ol, decan-1-ol, and dodecan-1-ol with cyclohexane at 303.15 K.

Experimental Section

The speeds of sound in pure liquids and in binary mixtures were measured with a multifrequency ultrasonic interferometer supplied by Mittal Enterprise, New Delhi. In the present work, a steel cell fitted with a guartz crystal of 2-MHz frequency was employed. The densities were measured with an Anton Paar vibrating-tube digital densimeter (model DMA 60/602) with a thermostated bath controlled to ±0.01 K. The details of the apparatus and procedure have been described in previous publications (Oswal and Palsanawala, 1989; Oswal and Phalak, 1993; Patel and Oswal, 1992).

Cyclohexane (Ranbaxy, AR) was dried over anhydrous $CaCl_2$ and fractionally distilled over Na. Ethanol (Alembic, LR), dried over molecular sieve type 4A (Fluka) was fractionally distilled twice, just before use. Propan-1-ol (E. Merck, AR), was refluxed over lime for 5 h and then distilled through a 1-m column. Butan-1-ol (BDH, AR), was washed with H_2SO_4 and with $NaHSO_4$ solution to remove bases, alkanals, and alkanones. Alkanoates were removed by boiling for 1.5 h with 20% NaOH (Riddick et al. 1986). It was dried with anhydrous K_2CO_3, followed by calcium oxide, and finally fractionally distilled through an efficient column. Pentan-1-ol (Merck-Schuchardt, AG), hexan-1-ol (Merck-Schuchardt, AG), heptan-1-ol (Merck-Schuchardt, AG), octan-1-ol (Fluka, AG), nonan-1-ol (Fluka, AG), decan-1-ol (Merck-Schuchardt, AG), and dodecan-1-ol (Koch-Light, AG) of purity better then 99.3 mol % were used as received without any purification except drying over molecular sieve 4A.

The purities of all the liquid samples were checked by measuring boiling points and by gas liquid chromatography analysis at Gujarat Insecticide Ltd, Ankleswar. The estimated purities of all the samples were better than 99.5% for alkanols and 99.9% for cyclohexane. Furthermore, the experimental densities and speeds of sound are compared with the literature values in Table 1. The agreement between the two is good.

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Table 1. Pure Component Properties at 303.15 K

	ρ/(kg·m^{-3})		u/(m·s^{-1})			
liquids	exptl	lit.	exptl	lit.	$10^3\alpha$/K^{-1}	C_P/(J·mol^{-1}·K^{-1})
cyclohexane	769.12	769.04,[a] 769.15[b]	1230	1229.1[b]	1.233	158.1
ethanol	780.69	780.64,[c] 780.69[d]	1134	1134[e]	1.096	112.4
propan-1-ol	795.62	795.61,[c] 795.88[f]	1179	1179[e]	1.025	143.9
butan-1-ol	801.90	801.91,[c] 801.93[f]	1223	1222[e]	0.976	177.1
pentan-1-ol	807.11	807.12,[c] 807.2[g]	1262	1263[h]	0.924	208.4
hexan-1-ol	811.95	811.95,[f] 812.01[d]	1287	1289[i]	0.885	242.9
heptan-1-ol	815.32	815.50,[d] 815.85[f]	1313	1313[i]	0.878	272.4
octan-1-ol	818.34	818.30,[d] 819.06[f]	1339		0.865	306.2
nonan-1-ol	822.40	821.03[f]	1354		0.843	338.5
decan-1-ol	822.92	822.85,[c] 822.90[f]	1366		0.829	373.0
dodecan-1-ol	826.77	826.20,[c] 826.58[f]	1388		0.821	438.4

[a] Stokes, R. H. *J. Chem. Thermodyn.* **1973**, *5*, 379. [b] Tamura, K.; Murakami, S.; Dio, S. *J. Chem. Thermodyn.* **1985**, *17*, 325. [c] Hales, J. L.; Ellender, J. H. *J. Chem. Thermodyn.* **1976**, *8*, 1177. [d] Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents Physical Properties and Methods of Purification*; Wiley Interscience: New York, 1986. [e] Freyer, E. B.; Hubbard, J. D.; Andrews, D. H. *J. Am. Chem. Soc.* **1929**, *51*, 759. [f] Diaz-Pena, M.; Tardajos, G. *J. Chem. Thermodyn.* **1979**, *11*, 441. [g] Garcia, B.; Herrera, C.; Lead, J. M. *J. Chem. Eng. Data* **1994**, *36*, 274. [h] Schaaffs, W. *Molecularakustic*; Springer Verlag: Berlin-Gottengen Hedelberg, 1983. [i] Aminabhavi, T. M.: Aralaguppi, M. I.; Harogoppad S. B.; Balungdi R. H. *J. Chem. Eng. Data* **1993,** *38*, 31.

Mixtures were prepared by mixing known masses of pure liquids in narrow-mouth ground glass stoppered bottles. All the mass measurements were performed on an electronic balance (Mettler AE 163, Switzerland) accurate to 0.01 mg. The possible error in the mole fraction is estimated to be less than $\pm 1 \times 10^{-4}$. The values of u and ρ were reproducible to within ± 1.0 m s^{-1} and ± 0.01 kg m^{-3}, respectively. The isentropic compressibilities determined from the relation $K_S = 1/(u^2\rho)$ are believed to be reliable to within 2.0 TPa^{-1}.

Results and Discussion

The results for the speed of sound u, density ρ, isentropic compressibility K_S, excess molar volume V^E, and excess isentropic compressibility K_S^E are given in Table 2.

K_S^E and V^E in each mixture were calculated from K_S and ρ of pure liquids and binary mixtures with following expression

$$Y^E = Y - Y^{id} \tag{1}$$

where Y is either K_S or V.

The V^{id} for an ideal mixture was calculated from usual relation

$$V^{id} = \sum x_i V_i^\circ = \sum x_i M_i/\rho_i \tag{2}$$

while K_S^{id} for an ideal mixture was calculated from the relation recommended by Benson and Kiyohara (1979) and Douheret et al., (1985)

$$K_S^{id} = \sum \phi_i \{K_{S,i}^\circ + TV_i^\circ(\alpha_i^\circ)^2/C_{P,i}^\circ\} - T\left(\sum x_i V_i^\circ\right)\left(\sum \phi_i \alpha_i^\circ\right)^2 \Big/ \left(\sum x_i C_{P,i}^\circ\right) \tag{3}$$

in which the V_i°, α_i°, and $C_{P,i}^\circ$ are, respectively, the molar volume, isobaric thermal expansion coefficient, and molar isobaric heat capacity of pure component i and $\phi_i = x_i V_i^\circ / \sum x_j V_j^\circ$ is the volume fraction of i in the mixture, stated in terms of the unmixed components. The values of α_i° and $C_{P,i}^\circ$ used for these calculations are listed in Table 1.

The mixing quantity Δu has been calculated as has been common in the literature (Kiyohara, et al., 1978; Tamura et al., 1983; Aicart et al., 1990) by

$$\Delta u = u - \sum_i x_i u_i^\circ \tag{4}$$

The estimated accuracy in the values of V^E and K_S^E is 5×10^{-9} m^3 mol^{-1} and 2.0 TPa^{-1}, respectively.

For compact and smooth representation, the values of u and K_S were fitted to a polynomial equation of the form

$$Y = \sum_{i=1}^{m} A_i x_1^{i-1} \tag{5}$$

where $Y = u$ and K_S.

The excess functions V^E and K_S^E and the mixing quantity Δu were smoothed to a Redlich–Kister (1948) polynomial regression of the type

$$\psi^E = x_1 x_2 \sum_{i=0}^{m} A_i (1 - 2x_1)^i \tag{6}$$

where $\psi^E = V^E$, K_S^E, and Δu.

The values of coefficients A_i of eqs 5 and 6 and the corresponding standard deviations σ obtained by the method of least squares, assigning equal weights to each point, are given in Tables 3 and 4. The standard deviations σ have been defined as

$$\sigma = \left[\frac{\sum (Y_{obs} - Y_{cal})^2}{n - m}\right]^{1/2} \tag{7}$$

where n and m represent the number of experimental points and numbers of coefficients used in eqs 5 and 6.

It can be seen from Figure 1 that the magnitude of positive deviations in K_S observed for ethanol + cyclohexane decreases as the chain length of alkanol is increased up to octan-1-ol. K_S varies almost linearly with mole fraction in case of octan-1-ol + cyclohexane. There is change of sign of deviations from nonan-1-ol onward. The magnitude of negative deviations increases from nonan-1-ol to dodecan-1-ol.

The values of V^E as shown in Figure 2 are positive for all the 10 mixtures investigated. The magnitude of V^E varies with the chain length of alkan-1-ol. With increasing length of alkan-1-ol, the maximum value of V^E decreases and its location shifts to lower mole fraction of alkan-1-ol.

Table 2. Experimental Densities, Speeds of Sound, Isentropic Compressibilities, and Excess Molar Volumes and for Alkan-1-ol + Cyclohexane at 303.15 K

x_1	ρ/(kg·m^{-3})	u/(m·s^{-1})	K_S/TPa^{-1}	10^9V^E/(m^3·mol^{-1})	x_1	ρ/(kg·m^{-3})	u/(m·s^{-1})	K_S/TPa^{-1}	10^9V^E/(m^3·mol^{-1})
(1) Ethanol + Cyclohexane									
0.0000	769.12	1230	859		0.5929	769.01	1161	964	537.8
0.0952	768.22	1218	877	207.2	0.7129	770.70	1150	981	480.9
0.1976	767.71	1205	897	358.4	0.7828	772.28	1144	989	405.8
0.2988	767.58	1193	915	455.1	0.9018	776.02	1137	996	224.7
0.3894	767.70	1183	930	512.4	1.0000	780.69	1134	996	
0.4879	768.10	1172	947	546.3					
(2) Propan-1-ol + Cyclohexane									
0.0000	769.12	1230	859		0.6115	779.60	1184	915	377.6
0.1090	769.59	1219	874	218.9	0.7080	782.74	1181	915	324.0
0.2080	770.63	1210	886	339.7	0.8094	786.46	1178	916	252.2
0.3385	772.70	1200	898	423.0	0.9188	791.38	1178	910	121.9
0.4215	774.52	1194	905	426.0	1.0000	795.62	1179	904	
0.5055	776.62	1189	910	411.6					
(3) Butan-1-ol + Cyclohexane									
0.0000	769.12	1230	859		0.6055	784.91	1209	871	343.1
0.1091	770.67	1221	870	212.6	0.7099	788.91	1210	865	284.1
0.2111	772.77	1217	873	327.8	0.8096	792.99	1213	857	213.7
0.2980	774.95	1214	875	380.0	0.8981	796.95	1217	847	126.2
0.4038	778.02	1211	876	399.3	1.0000	801.90	1223	833	
0.4890	780.79	1209	876	386.3					
(4) Pentan-1-ol + Cyclohexane									
0.0000	769.12	1230	859		0.6025	789.56	1231	835	336.6
0.0977	771.59	1225	863	175.1	0.7049	793.84	1236	824	281.4
0.2165	775.19	1222	863	302.3	0.7922	797.60	1242	812	219.7
0.3008	778.10	1222	860	341.8	0.9023	802.56	1251	796	113.2
0.4012	781.64	1223	855	378.3	1.0000	807.11	1260	779	
0.5004	785.49	1226	846	364.9					
(5) Hexan-1-ol + Cyclohexane									
0.0000	769.12	1230	859		0.6052	794.30	1252	803	322.8
0.1085	773.17	1229	856	173.8	0.7010	798.56	1259	790	272.9
0.2023	776.87	1231	849	278.8	0.7991	802.99	1268	774	194.8
0.3065	781.27	1234	840	334.5	0.8894	807.03	1276	761	113.8
0.3939	785.00	1238	831	360.1	1.0000	811.95	1287	743	
0.5019	789.71	1245	816	357.6					
(6) Heptan-1-ol + Cyclohexane									
0.0000	769.12	1230	859		0.6052	797.97	1271	775	313.5
0.0996	773.73	1232	851	176.0	0.7008	802.31	1281	759	265.3
0.1970	778.42	1237	839	281.2	0.7950	806.50	1291	743	199.4
0.3024	783.58	1244	824	337.1	0.8840	810.40	1300	730	118.3
0.3923	787.95	1251	810	353.0	1.0000	815.32	1313	710	
0.5062	793.35	1261	792	347.6					
(7) Octan-1-ol + Cyclohexane									
0.0000	769.12	1230	859		0.5414	798.34	1283	760	321.7
0.1206	775.99	1239	839	195.5	0.6080	801.47	1291	748	305.2
0.2210	781.65	1248	821	284.4	0.7550	808.13	1309	722	223.9
0.2975	785.84	1255	807	322.4	0.8637	812.79	1322	703	137.2
0.3517	788.74	1261	797	335.8	1.0000	818.34	1339	680	
0.4355	793.08	1270	781	341.2					
(8) Nonan-1-ol + Cyclohexane									
0.0000	769.12	1230	859		0.6055	805.43	1302	732	291.7
0.1050	776.47	1241	836	162.4	0.6959	809.71	1314	715	245.0
0.2105	783.41	1253	813	261.8	0.8010	814.36	1327	697	177.5
0.3110	789.58	1265	791	313.9	0.9054	818.70	1341	679	90.8
0.3969	794.52	1275	774	333.2	1.0000	822.40	1354	663	
0.4955	799.87	1288	753	325.9					
(9) Decan-1-ol + Cyclohexane									
0.0000	769.12	1230	859		0.5845	805.92	1310	723	295.4
0.1009	777.04	1243	832	143.1	0.6939	810.90	1325	702	252.6
0.1983	783.93	1256	808	239.7	0.7949	815.20	1339	684	179.3
0.2985	790.41	1271	783	293.9	0.8949	819.13	1352	667	94.3
0.3954	796.08	1284	761	323.6	1.0000	822.92	1366	651	
0.5000	801.74	1299	739	314.6					
(10) Dodecan-1-ol + Cyclohexane									
0.0000	769.12	1230	859		0.5985	811.39	1334	692	268.1
0.0858	777.62	1246	828	128.8	0.6982	815.84	1348	674	217.0
0.1621	784.32	1259	804	200.5	0.7746	818.93	1359	661	171.2
0.3050	794.89	1285	761	291.4	0.8620	822.17	1371	647	112.6
0.4050	801.19	1302	736	308.2	1.0000	826.77	1390	626	
0.5060	806.80	1319	712	298.2					

Table 3. Coefficients A_i of Eq 5 and Standard Deviations σ

property	A_0	A_1	A_2	A_3	A_4	σ
			(1) Ethanol + Cyclohexane			
$u/(m \cdot s^{-1})$	1229.7	−119.5	−20.8	44.2		0.5
K_S/TPa^{-1}	858.8	206.6	−112.6	200.7	−157.6	0.5
			(2) Propan-1-ol + Cyclohexane			
$u/(m \cdot s^{-1})$	1229.9	−102.6	34.6	17.0		0.3
K_S/TPa^{-1}	859.3	139.4	−57.5	−37.0		0.3
			(3) Butan-1-ol + Cyclohexane			
$u/(m \cdot s^{-1})$	1229.3	−70.4	55.2	8.7		0.6
K_S/TPa^{-1}	860.0	84.3	−104.0	−6.9		1.0
			(4) Pentan-1-ol + Cyclohexane			
$u/(m \cdot s^{-1})$	1229.8	−58.1	113.1	−25.0		0.3
K_S/TPa^{-1}	859.3	52.4	−179.6	47.5		0.5
			(5) Hexan-1-ol + Cyclohexane			
$u/(m \cdot s^{-1})$	1229.8	−14.3	102.6	−31.2		0.3
K_S/TPa^{-1}	859.5	−23.2	−149.9	57.0		0.7
			(6) Heptan-1-ol + Cyclohexane			
$u/(m \cdot s^{-1})$	1229.7	17.0	112.4	−46.4		0.3
K_S/TPa^{-1}	859.7	−83.7	−132.9	67.6		0.8
			(7) Octan-1-ol + Cyclohexane			
$u/(m \cdot s^{-1})$	1230.0	64.3	80.2	−35.7		0.4
K_S/TPa^{-1}	859.2	−162.6	−57.2	41.0		0.5
			(8) Nonan-1-ol + Cyclohexane			
$u/(m \cdot s^{-1})$	1229.9	103.6	32.6	−12.4		0.3
K_S/TPa^{-1}	859.2	−225.9	21.2	8.8		0.5
			(9) Decan-1-ol + Cyclohexane			
$u/(m \cdot s^{-1})$	1229.7	133.7	13.4	−10.9		0.4
K_S/TPa^{-1}	859.2	−277.3	81.4	−12.4		0.5
			(10) Dodecan-1-ol + Cyclohexane			
$u/(m \cdot s^{-1})$	1229.8	189.2	−24.5	−4.9		0.6
K_S/TPa^{-1}	859.1	−373.5	188.6	−47.9		0.5

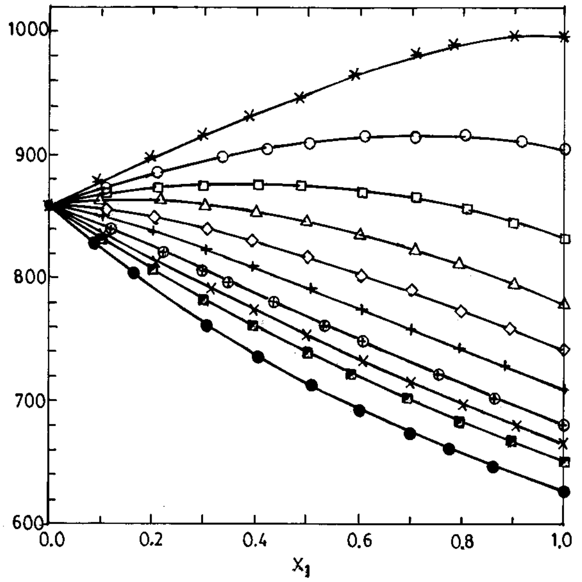

Figure 1. Isentropic compressibility for alkan-1-ol + cyclohexane at 303.15 K. Experimental points: C_2H_5OH (*), C_3H_7OH (○), C_4H_9OH (□), $C_5H_{11}OH$ (△), $C_6H_{13}OH$ (◇), $C_7H_{15}OH$ (+), $C_8H_{17}OH$ (⊕), $C_9H_{19}OH$ (×), $C_{10}H_{21}OH$ (◪), $C_{12}H_{25}OH$ (●). (−) calculated with eq 5.

The V^E for many of the systems have been reported in the literature. Most of the literature data were measured at 295.15 or at 298.15 K. Our experimental values and literature values of V^E interpolated to mole fraction 0.5 are listed in Table 5. For all of these systems, the present experimental values were very close to the values obtained from literature data. For the majority of systems discrepancies between literature values and present data is less than 3%; this may partly be due to the different temperatures.

Table 4. Coefficients A_i of Eq 6 and Standard Deviations σ

property	A_0	A_1	A_2	A_3	σ
		(1) Ethanol + Cyclohexane			
$10^9 V^E/(m^3 \cdot mol^{-1}$	2180.3	−211.8	441.8	200.1	2.5
$\Delta u/(m \cdot s^{-1})$	−45.9	23.6			0.5
K_S^E/TPa	134.1	−66.6	24.9		0.6
		(2) Propan-1-ol + Cyclohexane			
$10^9 V^E/(m^3 \cdot mol^{-1})$	1673.4	405.5	447.6		5.3
$\Delta u/(m \cdot s^{-1})$	−58.2	8.6			0.4
K_S^E/TPa^{-1}	78.9	−8.5			0.4
		(3) Butan-1-ol + Cyclohexane			
$10^9 V^E/(m^3 \cdot mol^{-1})$	1535.5	517.6	408.6		1.8
$\Delta u/(m \cdot s^{-1})$	−69.1	−2.3			1.0
K_S^E/TPa^{-1}	52.8	8.9			1.1
		(4) Pentan-1-ol + Cyclohexane			
$10^9 V^E/(m^3 \cdot mol^{-1})$	1466.8	410.5	261.6		4.9
$\Delta u/(m \cdot s^{-1})$	−75.8	−8.4			0.4
K_S^E/TPa^{-1}	40.7	15.5			0.6
		(5) Hexan-1-ol + Cyclohexane			
$10^9 V^E/(m^3 \cdot mol^{-1})$	1429.7	406.0	85.3		3.6
$\Delta u(m \cdot s^{-1})$	−54.3	−18.4	−3.9		0.3
K_S^E/TPa^{-1}	2.8	6.2			0.3
		(6) Heptan-1-ol + Cyclohexane			
$10^9 V^E/(m^3 \cdot mol^{-1})$	1391.2	389.9	261.2	190.3	1.7
$\Delta u/(m \cdot s^{-1})$	−45.1	−20.0			0.7
K_S^E/TPa^{-1}	−1.7	2.7			0.4
		(7) Octan-1-ol + Cyclohexane			
$10^9 V^E/(m^3 \cdot mol^{-1})$	1336.5	355.4	288.2	164.9	1.8
$\Delta u/(m \cdot s^{-1})$	−26.0	−15.7			0.2
$K_S^E/TPa^{-1})$	−16.6	−11.3			0.4
		(8) Nonan-1-ol + Cyclohexane			
$10^9 V^E/(m^3 \cdot mol^{-1})$	1296.9	410.1	155.2		1.4
$\Delta u/(m \cdot s^{-1})$	−14.3	−5.7			0.4
K_S^E/TPa^{-1}	−23.8	−31.2			0.6
		(9) Decan-1-ol + Cyclohexane			
$10^9 V^E/(m^3 \cdot mol^{-1})$	1279.7	286.9	27.1	121.6	4.2
$\Delta u/(m \cdot s^{-1})$	0.5				
$K_S^E/TPa^{-1})$	−31.2	−33.4			0.8
		(10) Dodecan-1-ol + Cyclohexane			
$10^9 V^E/(m^3 \cdot mol^{-1})$	1188.4	421.1	108.6		3.3
$\Delta u/(m \cdot s^{-1})$	30.9	−1.0	−10.8		0.4
$K_S^E/TPa^{-1})$	−32.0	−47.6	−29.7		1.0

Figures 3 and 4 show the plots of the experimental values and calculated curves according to eq 6 for Δu and K_S^E against mole fraction of alkan-1-ol. The values of Δu decrease with the number n of carbon atoms of the alkan-1-ols from 2 to 5 and then increase from 5 to 12, going from negative values for (pentan-1-ol + cyclohexane) to positive values for (dodecan-1-ol + cyclohexane). Change of sign for Δu occurs between mixture containing nonan-1-ol and decan-1-ol. The values of K_S^E in Figure 4 decrease with number carbon atoms of the alkan-1-ol going from positive values for ethanol + cyclohexane to negative for dodecan-1-ol + cyclohexane. The change of sign for K_S^E occurs between hexan-1-ol and heptan-1-ol. Our K_S^E values for pentan-1-ol + cyclohexane are lower by 7 TPa^{-1} at $x = 0.5$ than those of Orge et al. (1995). The trend of decreasing K_S^E with the chain length of alkan-1-ol is similar to that observed in case of V^E.

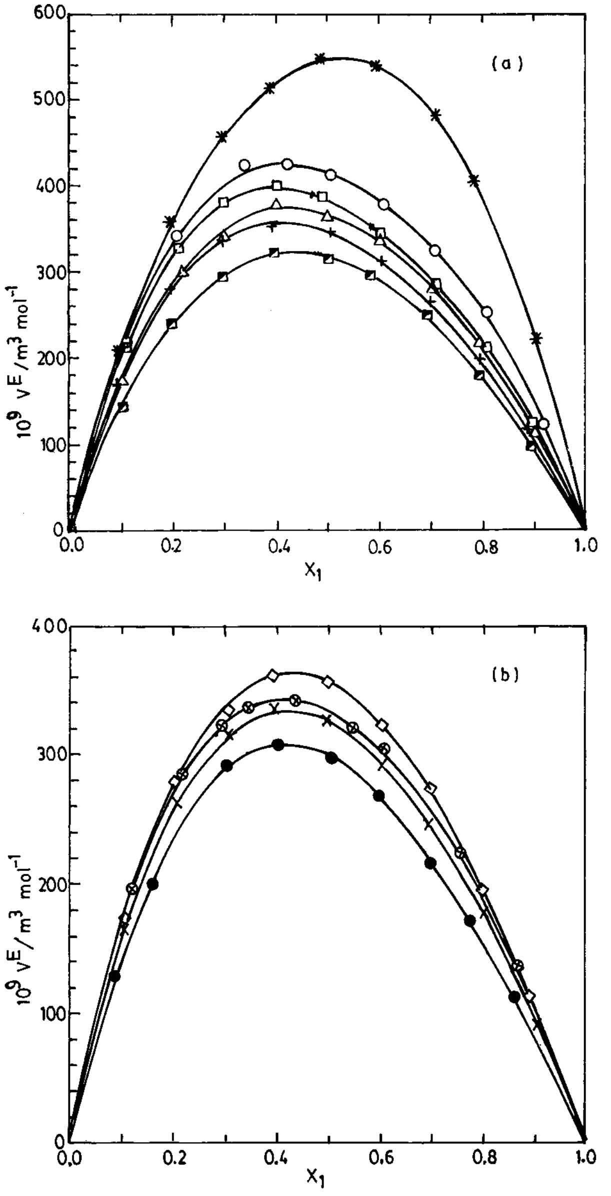

Figure 2. Excess molar volumes V^E for alkan-1-ol + cyclohexane at 303.15 K. Experimental points: (a) C_2H_5OH (*), C_3H_7OH (○), C_4H_9OH (□), $C_5H_{11}OH$ (△), $C_7H_{15}OH$ (+), $C_{10}H_{21}OH$ (◪); (b) $C_6H_{13}OH$ (◇), $C_8H_{17}OH$ (⊗), $C_9H_{19}OH$ (×), $C_{12}H_{25}OH$ (●). (—) calculated with eq 6.

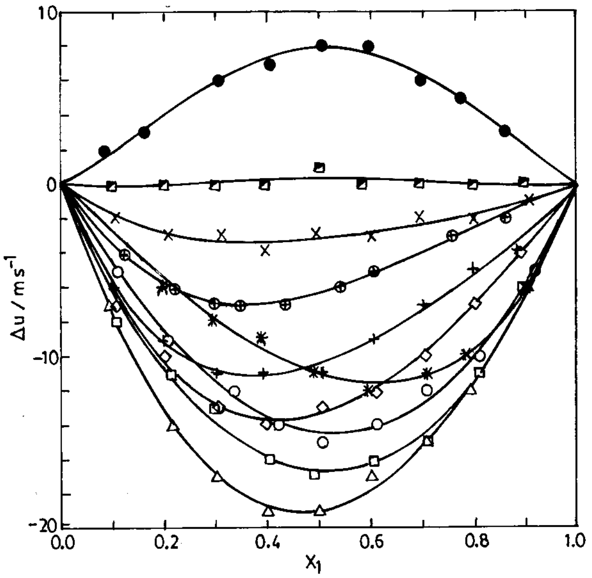

Figure 3. Deviations of speed of sound Δu for alkan-1-ol + cyclohexane at 303.15 K. Symbols same as in Figure 1. (—) calculated with eq 6.

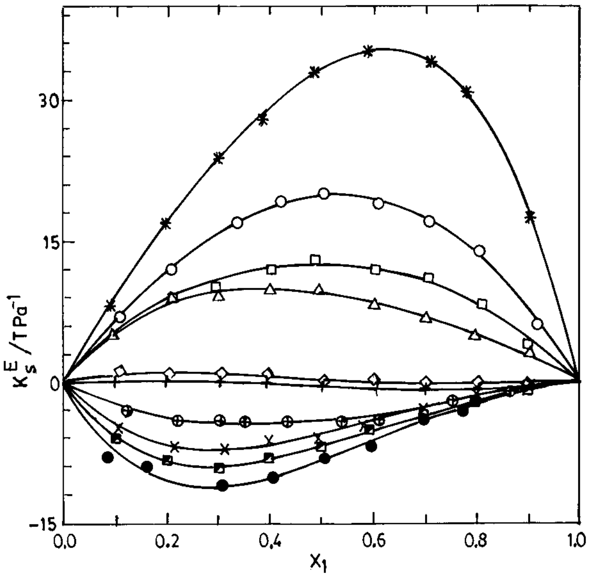

Figure 4. Excess isentropic compressibility K_S^E for alkan-1-ol + cyclohexane at 303.15 K. Symbols same as in Figure 1. (—) calculated with eq 6.

To arrive at certain meaningful conclusions for the present mixtures, it will be interesting to compare our volumetric data with those obtained for the mixtures of a 1-alkanol with hexane and/or heptane (Table 5). It is observed that V^E(cyclohexane) > V^E (hexane and/or heptane). This sequence is coherent as cyclohexane molecules are better order breakers (Bhattacharyya and Patterson, 1980) than the flexible hexane or heptane. Similar behavior is also manifested through the results obtained for the excess isentropic compressibilities K_S^E. The volumetric and compressibility behavior summarized above can be explained qualitatively by postulating that V^E and K_S^E are the resultant of opposite effects: (i) The self association of alkanols. Depolymerization of alkanols leads to increase in volume. As the extent of polymerization decreases by increase in chain length, the volume upon mixing decreases with the chain length of alkanol. (ii) The physical dipole−dipole interaction between alkanol monomers and multimers leads to increase in volume. (iii) The unfavorable interaction between the −OH group of an alkanol and $-CH_2-$ groups of cyclohexane leads to increase in volume. (iv) The difference in molar volumes or in free volumes between liquid components. Negative contributions arise from changes in 'free volume" in the real mixture (consisting of alkanol monomer, multimer, and cycloalkane molecule).

The combination of effects i to iii leads to positive contribution to V^E and K_S^E, while effect iv leads to contraction in the mixture resulting in negative V^E and K_S^E. The resultant values of V^E and K_S^E for present mixtures are due to the net effect of combination of i to iv. Furthermore, it appears that though both V^E and K_S^E are affected by all the four terms but to a different extent, so why are the values of K_S^E negative for some of mixtures while the values of V^E are positive.

Table 5. Comparison of Excess Molar Volumes at $x_1 = 0.5$ for Alkan-1-ol (1) + Component (2)[n]

	component (2)			
	cyclohexane		hexane	heptane
alkan-1-ol +	$10^9V^E_{\mathrm{exptl}}$	$10^9V^E_{\mathrm{lit.}}/\mathrm{m^3 \cdot mol^{-1}}$	$10^9V^E_{\mathrm{lit.}}/\mathrm{m^3 \cdot mol^{-1}}$	$10^9V^E_{\mathrm{lit.}}/\mathrm{m^3 \cdot mol^{-1}}$
ethanol	545.1	566(298.15)[a]	409(298.15)[e]	471.4(298.15)[f]
		565(298.15)[b]	463(308.15)[e]	523(308.15)[g]
		565(300.15)[c]		
		577(303.15)[d]		
propan-1-ol	418.3	400(295.15)[h]	179.7(298.15)[f]	296.4(298.15)[f]
		411(298.15)[b]	241.7(313.15)[j]	293.9(298.15)[k]
		390(323.15)[i]		337(303.15)[g]
butan-1-ol	388.9	390(295.15)[h]	43.1(298.15)[j]	188.1(298.15)[f]
		393(298.15)[b]	74.5(313.15)[j]	219(303.15)[g]
pentan-1-ol	367.7	378(298.15)[b]	−198(298.15)[g]	72.6(298.15)[f]
		363(298.15)[l]	−250(308.15)[g]	102(303.15)[g]
hexan-1-ol	357.4	358(298.15)[b]	−223.6(298.15)[j]	−24.6(298.15)[f]
		390(298.15)[m]	−247.5(308.15)[j]	−35(303.15)[g]
heptan-1-ol	347.8	350(298.15)[b]		
octan-1-ol	334.1	342(298.15)[b]	−430.9(298.15)[j]	−213.9(298.15)[f]
			−524.0(313.15)[j]	−295.0(303.15)[g]
nonan-1-ol	324.2	335(298.15)[b]		
decan-1-ol	319.9	328(298.15)[b]	−473.4(298.15)[j]	−353.2(298.15)[f]
			−589.7(298.15)[f]	
dodecan-1-ol	297.1	303(298.15)[b]		−449.4(298.15)[f]

[a] Pardo and Van Ness (1965). [b] Jansens and Ruel (1972). [c] Scatchard and Satkiewicz (1964). [d] Harms (1943). [e] Marsh and Burfitt (1975). [f] Treszczanowicz and Benson (1985). [g] Treszczanowicz (1992). [h] Klapproth (1940). [i] Brzostowski and Hardman (1963). [j] Heintz et al. (1986). [k] Keller et al. (1995). [l] Orge et al. (1995). [m] Franjo et al. (1994). [n] Present values are at 303.15 K. Values in parentheses represent temperature in K.

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