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Isentropic compressibilities of ternary systems with 1-alkanol as non-common component

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Abstract. New isentropic compressibility data are reported for four ternary mixtures, which contained methylethylketone and *n*-octane as common components. 1-propanol, 1-butanol, 1-pentanol and 1-hexanol, which form a homologous series, were used as non-common components. The deviation in isentropic compressibility has been computed from the experimental results and compressibility of ideal mixtures. The deviation is positive over the whole range of volume fraction in the four mixtures. The positive deviation suggests that the structure breaking effect of the components outweighs the structure making effect.

Keywords. Isentropic compressibility; interferometer; molar volume ; excess volume: volume fraction ; sound velocity.

1. Introduction

We report here isentropic compressibilities for four ternary systems : methylethylketone(1) + 1-alkanol(2) + *n*-octane(3) at 303·15 K. This is in continuation of our earlier work (Naidu and Naidu 1981) on isentropic compressibilities of ternary mixtures which contained *n*-heptane as one of the components. The alkanols used here include: 1-propanol, 1-butanol, 1-pentanol and 1-hexanol. While *n*-octane is capable of exerting structure breaking effect on self-associated alkanols, methylethylketone would be able to exert both structure breaking and structure making effects. Hence, the systems afford an opportunity to study the relative strengths of structure breaking and structure making of the common components. Further, the data included here are expected to throw light on the effect of *n*-alkane chain length on isentropic compressibility.

2. Experimental

The alcohols (BDH) were purified by the method described earlier (Rao and Naidu 1974). Methylethylketone (BDH) was purified by the method described earlier

Table 1. Densities of pure substances at 303·15 K.

Liquid	Present work ρ/g cm^{-3}	Literature ρ/g cm^{-3}
1-Propanol	0·79562	0·79567
1-Butanol	0·80202	0·80206
1-Pentanol	0·80762	0·80764
1-Hexanol	0·81198	0·81201
n-Octane	0·69445	0·69450
Methylethylketone	0·79449	0·79452

Table 2. Sound velocities and isentropic compressibilities of pure liquids at 303·15 K.

Liquid	u (ms^{-1})	K_s (TPa^{-1})
1-Propanol	1190	888
1-Butanol	1224	832
1-Pentanol	1257	784
1-Hexanol	1285	746
n-Octane	1148	1093
Methylethylketone	1170	920

(Reddy and Naidu 1977). *n*-Octane (Riedel) was dried over sodium and then fractionally distilled. The purities of the samples were checked by comparing the measured densities with those reported in the literature (Timmermans 1950). The numerical data are given in table 1. Densities were measured using a bicapillary pycnometer described earlier (Rao 1974).

Isentropic compressibilities were computed from ultrasonic sound velocity and density using the relation

$$K_{s_{123}} = u^{-2}\,\rho^{-1} \tag{1}$$

where $K_{s_{123}}$, u and ρ denote isentropic compressibility, sound velocity and density respectively of a ternary mixture. The values of $K_{s_{123}}$ were accurate to $\pm$ 2 TPa. Ultrasonic sound velocities were measured with a single crystal ultrasonic interferometer at a frequency of 2 MHz and the values were accurate to $\pm$ 0·15%. Further, sound velocities were measured at a constant temperature, 303·15 $\pm$ 0·01 K. The densities for ternary mixtures were calculated from the experimental V^E_{123} included in our earlier communication (Naidu and Naidu 1982). The relation

Table 3. Experimental values for the isentropic compressibilities of ternary mixtures at 303·15 K.

Volume fraction of mek ϕ_1	Volume fraction of 1-alkanol ϕ_2	ρ (g cm^{-3})	u (ms^{-1})	K_{s123} (TPa^{-1})	K_{s123} (TPa^{-1})
		Methylethylketone (1) + 1-propanol (2) + *n*-octane (3)			
0·7029	0·1145	0·77378	1163	956	8
0·5860	0·2206	0·77314	1164	955	9
0·5971	0·2356	0·77609	1168	945	4
0·4794	0·2991	0·77029	1165	957	8
0·4394	0·3335	0·76975	1169	951	3
0·3348	0·4860	0·77534	1173	937	2
0·3055	0·4780	0·77124	1172	944	2
0·2092	0·6196	0·77650	1175	933	4
		Methylethylketone (1) + 1-butanol (2) + *n*-octane (3)			
0·6972	0·1232	0·77552	1168	945	5
0·5944	0·2396	0·77805	1172	936	8
0·4864	0·3418	0·77812	1174	932	12
0·3850	0·4245	0·77680	1175	923	8
0·3378	0·4926	0·77950	1182	918	12
0·3059	0·4907	0·77602	1183	921	9
0·2294	0·6042	0·78090	1190	904	8
0·1329	0·6897	0·78050	1194	899	9
		Methylethylketone (1) + 1-pentanol (2) + *n*-octane (3)			
0·7080	0·1114	0·77586	1152	971	35
0·5971	0·2365	0·77937	1164	947	30
0·4741	0·3081	0·77501	1176	933	17
0·4637	0·3510	0·77885	1182	919	15
0·3433	0·4733	0·78058	1192	902	14
0·3082	0·4773	0·77768	1186	914	22
0·2290	0·5959	0·78337	1199	888	19
0·1060	0·7143	0·78480	1210	870	16
0·0995	0·7493	0·78821	1211	865	21
		Methylethylketone (1) + 1-hexanol (2) + *n*-octane (3)			
0·7055	0·1115	0·77596	1154	968	36
0·5991	0·2367	0·78046	1164	946	39
0·5243	0·2839	0·77843	1176	929	25
0·4735	0·3454	0·78080	1182	917	26
0·4196	0·3831	0·77989	1181	919	31
0·3365	0·4813	0·78340	1200	887	19
0·2247	0·6151	0·78825	1216	858	17
0·1026	0·7129	0·78753	1225	846	18
0·1112	0·7519	0·79311	1230	833	20

$$\rho = \frac{x_1 M_1 + x_2 M_2 + x_3 M_3}{V + V^E_{123}} \tag{2}$$

was used in these calculations. x_1, x_2, x_3 and M_1, M_2, M_3 denote the mole fractions and molecular weights of methylethylketone, 1-alkanol and n-octane respectively. V and V^E_{123} denote molar volume and excess volume respectively.

3. Results

The deviation in isentropic compressibility, ΔK_{s123}, for a ternary mixture is computed from the relation :

$$\Delta K_{s_{123}} = K_{s_{123}} - K^{id}_{s_{123}} \tag{3}$$

where $K_{s_{123}}$ and $K^{id}_{s_{123}}$ are isentropic compressibilities of the real mixture and an ideal mixture respectively. The ideal isentropic compressibility is calculated using the relation

$$\Delta K_{s_{123}} = \phi_1 K_{s,1} + \phi_2 K_{s,2} + \phi_3 K_{s,3} \tag{4}$$

where ϕ_1, ϕ_2, ϕ_3 and K_{s_1}, K_{s_2}, K_{s_3} are volume fractions and isentropic compressibilities of methylethylketone, an alkanol and n-octane respectively. Isentropic compressibility of an ideal mixture is assumed to be additive in terms of volume fraction. Sound velocities and isentropic compressibilities of pure liquids are given in table 2. The experimental data for the mixtures are given in table 3.

The results in table 3 show that the deviation in isentropic compressibility is positive over the whole range of composition in the four ternary mixtures. The values of ΔK_{s123} for the four mixtures fall in the order:

1-propanol < 1-butanol < 1-pentanol < 1-hexanol.

The order suggests that increase in chain length of the alcohols contributes to an increase in the deviation of ΔK_{s123}.

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Explanation of symbols used

ρ	density, g cm^{-3}
u	sound velocity, ms^{-1}
K	absolute temperature
V	ideal molar volume, cm^3
K_{si}	isentropic compressibility of ith component in its pure state, TPa^{-1}

$K_{s_{123}}$	isentropic compressibility of the real ternary mixture, TPa^{-1}
$K^{id}_{s_{123}}$	isentropic compressibility of an ideal ternary mixture, TPa^{-1}
$\Delta K_{s_{123}}$	deviation in isentropic compressibility of the ternary mixture, $(K_{s_{123}} - K^{id}_{s_{123}})$
V^E_{123} (exp)	experimental excess volume of ternary systems, $cm^3\ mol^{-1}$
m_i	molecular weight of *i*th component in the ternary mixture
ϕ_i	volume fraction of *i*th component in the ternary mixture
x_i	mole fraction of *i*th component in the ternary mixture

Subscripts

1, 2, 3, components

Superscripts

E excess property

id ideal

Parentheses

exp experimental

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