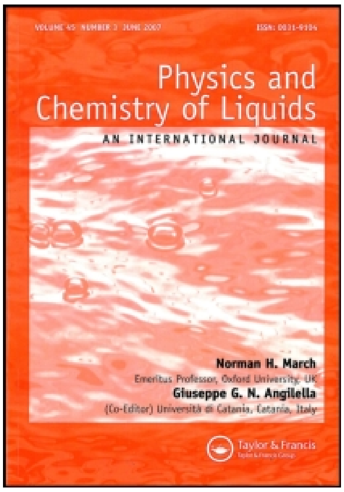

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Ultrasonic Speeds and Isentropic Compressibilities of Ternary Liquid Mixtures at 303.15 K

K. Mohankrishnan[a]; K. Rambabu[a]; D. Ramachandran[a]; G. K. Raman[a]
[a] Department of Chemistry, College of Engineering, Sri Venkateswara University, Tirupati

To cite this Article Mohankrishnan, K. , Rambabu, K. , Ramachandran, D. and Raman, G. K.(1995) 'Ultrasonic Speeds and Isentropic Compressibilities of Ternary Liquid Mixtures at 303.15 K', Physics and Chemistry of Liquids, 29: 4, 257 — 262
To link to this Article: DOI: 10.1080/00319109508031643
URL: http://dx.doi.org/10.1080/00319109508031643

Phys. Chem. Liq., 1995, Vol. 29, pp. 257–262
Reprints available directly from the publisher
Photocopying permitted by license only

ULTRASONIC SPEEDS AND ISENTROPIC COMPRESSIBILITIES OF TERNARY LIQUID MIXTURES AT 303.15K

K. MOHANKRISHNAN, K. RAMBABU,
D. RAMACHANDRAN and G. K. RAMAN

Department of Chemistry, College of Engineering, Sri Venkateswara University, Tirupati 517 502

(Received 29 December 1994)

Measurements of ultrasonic speed were carried out for (2-methoxyethanol (1) + Ethylacetate (2) + benzene (3); + toluene (3); + chlorobenzene (3); + bromobenzene (3); and + nitrobenzene (3); at 303.15 K. The ultrasonic speeds of these mixtures were also evaluated on the basis of Jacobson's free length theory (FLT) and Schaaff's Collission factor theory (CFT). The theoretical and experimental values is fair for all the mixtures. An attempt has also been made to explain the nature of intermolecular interactions in the light of isentropic compressibilities.

KEY WORDS: Ternary mixtures: sound velocity: intermolecular forces.

1 INTRODUCTION

In the chemical literature, properties of binary systems are relatively abundant, properties of ternary systems are scarce. Mixtures of associated liquids generally show nonideal behaviour in respect of properties like excess volume and isentropic compressibility. This work forms part of a study of thermodynamic properties[1] of pure liquids and liquid mixtures are of interest both to chemists and to chemical engineers for processing of petroleum and petrochemical products. The present study was undertaken to determine the isentropic compressibility from ultrasonic speed and the density evaluated from excess volumes. Further, the third component brings a change in both the nature and degree of interaction between pairs of molecules. We present here experimental data for the isentropic compressibility of five ternary mixtures, 2-methoxyethanol (1) + Ethylacetate (2) + benzene, + toluene, + chlorobenzene, + bromobenzene and + nitrobenzene. Further the sound velocity data have been analysed in terms of free length theory[2] (FLT) and collision factor theory[3] (CFT). The theoretical aspects of FLT and CFT have been described in detail by Mohankrishnan *et al*[4].

2 EXPERIMENTAL

The liquids were purified as described earlier[1]. The purity of the samples was checked by comparing the measured densities of the components with those reported in the literature[5,6]. Sound velocity was measured with a single-crystal interferometer at a frequency of 3 MHZ and the data were accurate to within $\pm 0.15\%$. All the measurements were made at constant temperature employing a thermostat that could be maintained to ± 0.01 K.

Isentropic compressibilities were computed from the measured sound velocity and the density, evaluated from excess volume measurements. Isentropic compressibilities calculated from the sound velocity and density are accurate to ± 2 TPa^{-1}.

3 RESULTS AND DISCUSSION

Sound Velocity—The surface area Y and collision factor S of the pure components used in FLT and CFT were calculated using the experimental sound velocities and densities. Critical temperature, surface tension and the ratio of specific heats which are used in the calculation of molar volume at absolute zero V_0 and the average molecular radius r_m were taken from the literature[6,7-9]. The values of molar volume V_1 available volume V_a, free length L_f, surface area Y, collision factor (S), and the average radius of the molecules of the pure components are given in Table 1. Sound velocity data predicted in terms of FLT and CFT are given in Table 2 along with experimental results.

The experimental and predicted (FLT and CFT) sound velocities are in good agreement in all the systems studied.

Isentropic compressibility — Isentropic compressibilities of ternary mixtures, K_{s123}; were calculated using the expression.

$$K_{s123} = u^{-2} \rho^{-1} \tag{1}$$

Where U and ρ denote the sound velocity and density respectively.

The densities for ternary mixtures were calculated from the relation.

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

Where x_1, x_2 and x_3 and M_1, M_2, and M_3 denote the mole fractions and molecular weights of 2-methoxyethanol, ethylacetate and aromatic hydrocarbon respectively.

Table 1 Molar volume, V, molar volume at absolute zero V_0, available volume V_a, Free Length L_f, Surface area Y, Collission factor S, and average molecular radius r_m of the pure liquid components at 303.15 K.

Component	V cm³/mol	V_0 cm³/mol	V_a cm³/mol	L_f A⁰	Y	S	r_m A⁰
2-methoxyethanol	79.6217	62.8798	16.7419	0.4846	69.0957	1.7633	2.4607
Ethylacetate	99.1559	41.7090	57.4469	0.5966	192.5810	1.5381	2.6168
Benzene	89.9253	71.2689	18.6564	0.5293	70.4947	1.7214	2.5485
Toluene	103.4168	52.3850	55.0318	0.5302	207.5889	1.6981	2.7206
Chlorobenzene	102.7457	53.4892	49.2565	0.4819	204.4262	1.6210	2.6982
Bromobenzene	105.9780	58.0376	47.9404	0.4584	209.1641	1.4431	2.7402
Nitrobenzene	103.1530	60.4420	42.7110	0.4011	212.9693	1.7953	2.7367

Table 2 Volume fractions (ϕ_1) of 2-methoxyethanol (1) + Ethylacetate (2) with aromatic hydrocarbons (3), density (ρ), sound speed (u_{expt}), predicted from FLT (u), CFT (u), isentropic compressibility (from Eq. 1) and deviation in isentropic compressibility ΔK_s (from Eq. 3) at 303.15 K respectively.

Volume fraction of 2-methoxy-ethanol(ϕ_1)	*Volume fraction of aromatic hydro-carbon (ϕ_3)*	ρ $g \cdot cm^{-3}$	u_{exp} ms^{-1}	u_{FLT}	u_{CFT}	k_{s123}	K_{s123}	K'_{s123} TPa^{-1}	dK_{s123}
2-Methoxyethanol (1) + Ethylacetate (2) + benzene (3)									
0.1036	0.0908	0.89167	1139	1136	1162	864	19	6	13
0.0967	0.2122	0.88814	1157	1147	1179	841	17	8	9
0.1215	0.3117	0.88697	1178	1161	1201	812	14	9	5
0.0594	0.3750	0.88266	1179	1160	1197	815	10	10	0
0.1138	0.5081	0.88227	1205	1187	1229	781	18	12	6
0.0873	0.5603	0.88012	1207	1191	1232	780	19	13	6
0.0907	0.7043	0.87775	1221	1220	1254	764	31	14	17
0.0870	0.8017	0.87613	1239	1245	1268	744	29	13	16
0.1008	0.8478	0.87634	1249	1266	1277	731	29	14	15
2-Methoxyethanol (1) + Ethylacetate (2) + toluene (3)									
0.0843	0.0872	0.89048	1146	1141	1155	855	3	0	3
0.0747	0.2611	0.88464	1170	1167	1180	826	4	−5	9
0.0691	0.3774	0.88094	1185	1185	1196	808	5	−6	11
0.1184	0.4155	0.88246	1194	1198	1215	795	15	−3	18
0.0975	0.5359	0.87760	1206	1216	1229	783	19	3	16
0.1105	0.6747	0.87407	1241	1243	1255	743	9	14	−5
0.1137	0.6962	0.87360	1246	1247	1260	737	8	15	−7
0.0895	0.8015	0.86890	1257	1263	1272	728	12	16	−4
0.1000	0.8611	0.86759	1268	1276	1284	717	15	19	−4
2-Methoxyethanol (1) + Ethylacetate (2) + Chlorobenzene (3)									
0.0819	0.1194	0.91819	1143	1140	1157	834	2	−6	−2
0.0905	0.2339	0.94287	1170	1154	1173	775	−19	−11	−8
0.1021	0.2858	0.95441	1173	1162	1182	761	−13	−13	0
0.0834	0.3770	0.97271	1182	1171	1190	736	−15	−15	0
0.0928	0.4784	0.99444	1188	1187	1205	713	−4	−13	9
0.0677	0.5973	1.01784	1200	1200	1214	682	−6	−13	7
0.0920	0.6864	1.03684	1215	1219	1232	653	0	−7	7
0.0880	0.7997	1.05979	1230	1238	1246	624	5	−2	7
0.0919	0.8681	1.07327	1242	1251	1256	604	8	3	5
2-Methoxyethanol (1) + Ethylacetate (2) + bromobenzene (3)									
0.0810	0.1135	0.95874	1142	1119	1144	800	−28	−13	−15
0.0598	0.2518	1.03970	1132	1141	1141	751	−33	−27	−6
0.0904	0.3178	1.07867	1140	1115	1150	713	−37	−30	−7
0.0423	0.3887	1.12113	1124	1106	1139	706	−33	−36	3
0.0354	0.4895	1.18123	1125	1105	1138	669	−35	−39	4
0.0859	0.6270	1.26430	1131	1121	1153	618	−20	−32	12
0.0915	0.6920	1.30383	1133	1126	1155	597	−16	−27	11
0.0914	0.7848	1.35940	1134	1134	1156	572	−7	−19	12
0.0735	0.8673	1.40663	1140	1138	1152	547	−7	−10	3
2-Methoxyethanol (1) + Ethylacetate (2) + nitrobenzene (3)									
0.0896	0.0860	0.91813	1161	1149	1169	808	−17	−16	−1
0.0981	0.1598	0.94000	1191	1169	1193	750	−36	−32	−4
0.0826	0.2669	0.97272	1215	1195	1221	696	−42	−53	11
0.1045	0.3648	1.00303	1252	1229	1257	636	−47	−64	17
0.0796	0.5711	1.06817	1317	1291	1316	540	−50	−59	9
0.0874	0.6628	1.09699	1341	1328	1347	507	−36	−40	4
0.1011	0.7690	1.13049	1385	1379	1385	461	−25	−16	−9
0.0847	0.8307	1.14760	1392	1400	1402	450	−11	−6	−5
0.1001	0.8573	1.15632	1410	1420	1414	435	−8	0	−8

$V = \sum x_i V_i^0$ where V_i^0 is the molar volume of pure component i and V_{123}^E is the experimental excess molar volume. The deviation in isentropic compressibility, K_{s123} for a ternary mixture was computed employing the relation

$$K_{s123} = k_{s123} - k_{s123}^{id} \quad (3)$$

Where k_{s123} and k_{s123}^{id} are isentropic compressibilities of the real and an ideal mixture, respectively. The ideal isentropic compressibility was assumed to be additive in terms of volume fraction and was calculated using the relation

$$k_{s123}^{id} = \phi_1 k_{s1} + \phi_2 k_{s2} + \phi_3 k_{s3} \quad (4)$$

Where ϕ_1, ϕ_2 and ϕ_3 and k_{s1}, k_{s2}, and k_{s3} are volume fractions and isentropic compressibilites of 2-methoxyethanol, ethylacetate, and aromatic hydrocarbon, respectively.

The quantity dK_{s123}, the difference between the measured value and that computed from constituent binary data, was calculated as shown below

$$dK_{s123} = K_{s123} - K'_{s123} \quad (5)$$

Where K_{s123} is the deviation in isentropic compressibility calculated from experimenal data and K'_{s123} is the deviation calculated from binary data. The latter quantity was calculated using the relation

$$K'_{s123} = k_{s12} + k_{s13} + k_{s23} \quad (6)$$

Where k_{s12}, k_{s13} and k_{s23} denote deviations in isentropic compressibilities of the binary data. k_{sij} for a binary mixture was estimated using the smoothing equation

$$k_{sij} = \phi_i \phi_j [a_0 + a_1(\phi_i - \phi_j) + a_2(\phi_i - \phi_j)^2] \quad (7)$$

Where a_0, a_1 and a_2 are constants obtained by the method of least squares.

Further, the binary parameters for the deviation in isentropic compressibility to compute ternary data for mixtures of 2-methoxyethanol with aromatic hydrocarbons, 2-methoxyethanol with ethylacetate and ethylacetate with aromatic hydrocarbons were taken from the literature[4,10,11]. These parameters are given in Table 3 along with the standard deviation $\sigma(\Delta K_s)$.

Sound velocity data predicted in terms of FLT and CFT along with experimental sound velocity, isentropic compressibility, k_{s123}, and the deviation in insentropic compressibility, K_{s123}, for the ternary mixtures are given in Table 2. Finally the quantity dK_{s123} is also given in Table 2. An examination of results included in Table 2 shows that the values of dk_{s123} are non zero. This suggests that the ternary mixtures are not ideal in terms of constituent binaries. This shows that the third component modifies both the nature and degree of interaction between molecules of components.

Table 3 Values of the parameters a_0, a_1 and a_2 and the standard deviation σ (ΔK_s) for binary systems at 303.15 K.

System	a_0	a_1	a_2	$\sigma(\Delta K_s)$
	TPa^{-1}			
2-Methoxyethanol + benzene	100.980	−104.180	−68.171	1
2-Methoxyethanol + toluene	87.390	−111.425	13.862	1
2-Methoxyethanol + chlorobenzene	75.084	−55.348	−88.164	2
2-Methoxyethanol + bromobenzene	18.931	−33.536	−80.125	1
2-Methoxyethanol + nitrobenzene	−75.577	−86.365	80.081	1
2-Methoxyethanol + ethylacetate	−58.566	−61.817	48.925	1
Ethylacetate + benzene	31.389	1.188	35.915	1
Ethylacetate + toluene	−30.858	68.137	95.731	2
Ethylacetate + chlorobenzene	−79.999	9.176	7.646	2
Ethylacetate + bromobenzene	−166.083	−24.236	−15.560	2
Ethylacetate + nitrobenzene	−309.154	77.075	253.349	1

Table 4 Values of ternary constants A', B', C' and the standard deviation $\sigma(dK_{s123})$ of ternary systems at 303.15 K.

System	A'	B'	C'	$\sigma(dK_{s123})$
	TPa^{-1}			
2-methoxyethanol (1) + ethylacetate (2) + benzene (3)	56	10556	415937	2
2-methoxyethanol (1) + ethylacetate (2) + toluene (3)	173	12548	47010	4
2-methoxyethanol (1) + ethylacetate (2) + chlorobenzene	414	22525	−275844	3
2-methoxyethanol (1) + ethylacetate (2) + bromobenzene (3)	825	−12196	−202694	3
2-methoxyethanol (1) + ethylacetate (2) + nitrobenzene (3)	936	−9883	−374404	4

The algebraic values of dK_{s123} fall in the order

toluene > benzene ≈ nitrobenzene > bromobenzene > chlorobenzene.

This shows that there is no simple correlation between the substituted benzenes and dK_{s123}. The dK_{s123} values are positive for 2-methoxyethanol (1) + Ethylacetate (2) + benzene (3) over the entire range of composition and sigmoid for the mixtures of + toluene (3), + chlorobenzene (3), + bromobenzene (3), and + nitrobenzene (3). The negative $d(K_{s123})$ values arise from changes of 'free volume' in real mixtures and the presence of π electrons in substituted benzenes resulting in the formation of weak intermolecular complexes. The positive values of dK_{s123} arise due to breaking of hydrogen bonds in self-associated alkoxyalcohol. However, the net contribution will depend upon the relative ability of the common component to depolymerize and to form intermolecular complexes. The dK_{s123} values were fitted to the polynomial

$$dK_{s123} = \phi_1\phi_2\phi_3[A' + B'\phi_1(\phi_2 - \phi_3) + C'\phi_1^2(\phi_2 - \phi_3)^2] \tag{8}$$

Where ϕ_1, ϕ_2, and ϕ_3 are the volume of fractions of components 1, 2, and 3, respectively. The values adjustable parameters A', B', and C' are obtained by the least squares method and are given in Table 4 along with the standard deviation $\sigma(dK_{s123})$.

Acknowledgements

The authors Dr. K. Rambabu and K. Mohan Krishnan are grateful to the C.S.I.R. Research Associateship and S.V. University Fellowship respectively.

References

1. K. Mohan Krishnan, K. Rambabu, D. Ramachandran and G. K. Raman, Indian Council of Chemists (In press).
2. B. Jacobson, *J. Chem. Phys.*, **20**, 927 (1952).
3. W. Schaafs, *Z. Phys.*, **115**, 69 (1940).
4. K. Mohan Krishnan, K. Rambabu, D. Ramachandran, and G. K. Raman, Acta ciencia Indica (In press).
5. J. A. Riddick, W. B. Bunger and T. K. Sakano, Organic solvents Techniques of chemistry, 4th ed., John Wiley and Sons, New York Vol. II (1986).
6. J. Timmermans, Physico-chemical constants of pure organic compounds (Elsevier Publishing Co.,) Amsterdam, (1950).
7. International Critical Tables of numerical data; Physics, Chemistry and technology (McGraw-Hill, New York), (1930).
8. A hand book of chemistry and physics (CRC Graw Wood Parkway, Ohio) 58th edition (1977–78).
9. A. P. Kudchadker, A. B. Zwotinki, *J. Chem. Rev.*, **67**, 659 (1968).
10. H. Iloukhani, Ph. D. Thesis, S. V. University, Tirupati (1985).
11. K. M. Krishnan, K. Rambabu, P. Venkateswarlu and G. K. Raman, *J. Chem. Eng.* Data, **40**, 132 (1995).