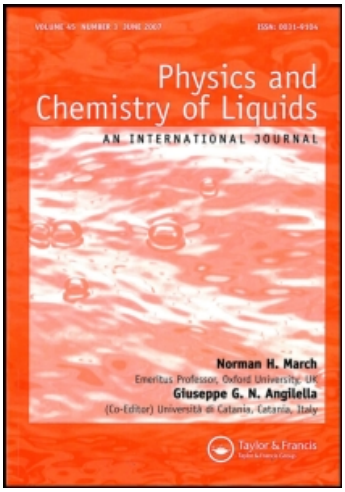

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Ultrasonic studies of *N*,*N*-dimethylformamide + cyclohexanone + 1-alkanols at 303.15 K

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Isentropic compressibilities (k_s) and deviation in isentropic compressibilities (k'_s) have been determined from the measurements of ultrasonic sound velocity (u) and densities (ρ) for the ternary mixtures of *N*,*N*-dimethylformamide (DMF), and cyclohexanone with 1-propanol, 1-butanol, 1-pentanol and 1-hexanol at 303.15 K. The relative magnitude and sign of k'_s have been interpreted in terms of possible molecular interactions between the unlike molecules. The deviation in k'_s values are negative throughout the range of volume fraction in all four ternary mixtures.

Keywords: Isentropic compressibility; Density; *N*,*N*-Dimethylformamide; Cyclohexanone; 1-Alkanols

1. Introduction

In recent years, much effort has been made with the measurement and interpretation of the ultrasonic properties of liquids and liquid mixtures. The ultrasonic studies are of great importance in helping to understand the nature and extent of the patterns of molecular aggregation that exist in liquid mixtures, resulting from intermolecular interactions [1–4]. *N*,*N*-dimethylformamide (DMF) is stable and highly polar, non-aqueous compound representative of amidic solvent. This amide is widely used in settings such as solvent reactivity relationships. DMF as a pure solvent is certainly to some extent associated by means of dipole–dipole interactions, and is of particular interest because any significant structural effects are absent due to the lack of hydrogen bonds; therefore it may work as an aprotic protophilic solvent of large dipole moment

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and high dielectric constant ($\mu = 3.24$ D and $\varepsilon = 36.71$ at 298.15 K) [5]. On the other hand, alkanols are polar liquids, strongly self-associated by hydrogen bonding to extents of polymerization that may differ depending on temperature, chain length and position of the OH group. Alkanol size, chain length and internal pressure (which is related to density and refractive index) are important parameters that must be taken into account to explain the behavior of the DMF, cyclohexanone with 1-alkanols mixtures. A survey of the literature reveals that no ultrasonic studies for the ternary systems of DMF + cyclohexanone + 1-alkanols, namely, 1-propanol, 1-butanol, 1-pentanol and 1-hexanol, and hence the investigation has been made at 303.15 K for these ternary mixtures.

2. Experimental

2.1. *Materials*

All the chemicals used were of analytical grade and purchased from commercial sources. They were further purified by standard procedures [5]. The purity of compounds were checked by comparing the measured densities (ρ) and ultrasonic sound velocity (u) with those reported in literature [5,6].

2.2. *Apparatus and procedure*

The densities of all pure components were determined by a bicapillary pycnometer with an accuracy of two parts in 10^5. The measured u and ρ and those reported in the literature are listed in table 1. The mixtures were prepared by mixing weighed amount of pure liquids.

The u of liquids and mixtures was measured with multi-frequency ultrasonic interferometer supplied by Mittal Enterprise, New Delhi. In the present work, a steel cell fitted with a quartz crystal of 2 MHz frequency was employed and the values are accurate to 0.02%. The temperature was maintained by circulating water around the liquid cell, controlled thermostatically at 303.15 ± 0.01 K. The details of the experimental procedure have already been described elsewhere [7,8].

The isentropic compressibility of ternary mixtures (k_{s123}) was calculated from the expression:

$$k_{s123} = u_{123}^{-2}\rho_{123}^{-1} \tag{1}$$

Table 1. Ultrasonic sound velocities (u) and densities (ρ) of the pure compounds at 303.15 K.

	u (m s^{-1})		ρ (g cm^{-3})	
Component	Expt.	Lit. [11,18]	Expt.	Lit. [5,6]
DMF	1462	1462	0.94118	0.94120
Cyclohexanone	1387	1388	0.93758	0.93761
1-Propanol	1189	1191	0.79601	0.79600
1-Butanol	1226	1224	0.80203	0.80206
1-Pentanol	1258	1256	0.80761	0.80764
1-Hexanol	1284	1287	0.81203	0.81201

where u_{123} and ρ_{123} denotes ultrasonic velocity and density of ternary mixtures, respectively. The density of ternary mixtures was computed using the relation:

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

where x_1, x_2 and x_3 denote the mole fractions of the three components and M_1, M_2 and M_3 are the molar masses. V is the molar volume and V^{E} the excess volume of the mixture. The ternary excess volumes for the *N*,*N*-dimethylformamide (DMF) + cyclohexanone + 1-alkanols at 303.15 K have already been published in our earlier paper [9].

The deviation in isentropic compressibility $k'_{\mathrm{s}123}$ was estimated using the relation:

$$k'_{\mathrm{s}123} = k_{\mathrm{s}123} - \phi_1 k_{\mathrm{s}1} - \phi_2 k_{\mathrm{s}2} - \phi_3 k_{\mathrm{s}3} \tag{3}$$

where ϕ_1, ϕ_2, ϕ_3 and $k_{\mathrm{s}1}$, $k_{\mathrm{s}2}$, $k_{\mathrm{s}3}$ are volume fractions and isentropic compressibilities of the three pure compounds. The quantity $\Delta k_{\mathrm{s}123}$ the difference between the measured value of $k'_{\mathrm{s}123}$ and that of computed from binary data $k'_{\mathrm{s}123(\mathrm{b})}$ has been calculated using the relation:

$$\Delta k_{\mathrm{s}123} = k'_{\mathrm{s}123} - k'_{\mathrm{s}123(\mathrm{b})} \tag{4}$$

The latter quantity was computed using Redlich–Kister [10] relation using the binary parameters:

$$k'_{\mathrm{s}123(\mathrm{b})} = k'_{\mathrm{s}12} + k'_{\mathrm{s}13} + k'_{\mathrm{s}23} \tag{5}$$

where $k'_{\mathrm{s}12}$, $k'_{\mathrm{s}13}$ and $k'_{\mathrm{s}23}$ denote the deviation in isentropic compressibilities for the three binary mixtures and these are estimated using the smoothing equation.

$$k'_{sij} = \phi_i \phi_j [b_0 + b_1(\phi_i - \phi_j) + b_2(\phi_i - \phi_j)^2] \tag{6}$$

where, b_0, b_1 and b_2 are constants obtained by the methods of least squares. Further the binary parameters for the mixtures of DMF with 1-alkanols [11], cyclohexanone with 1-alkanols [12] and DMF + cyclohexanone [13] were taken from literature. These parameters for all the binary mixtures are presented in table 2.

Table 2. Values of binary parameters b_0, b_1, b_2 and the standard deviation $\sigma(k'_{\mathrm{s}})$ for binary systems at 303.15 K.

	$\mathrm{T\,Pa^{-1}}$			
System[a]	b_0	b_1	b_2	$\sigma(k'_{\mathrm{s}})$
DMF + 1-propanol	−225.6	35.6	89.5	2
DMF + 1-butanol	−92.3	−16.5	69.1	1
DMF + 1-pentanol	37.2	8.8	−5.9	1
DMF + 1-hexanol	37.6	107.4	−2.8	1
Cyclohexanone + 1-propanol	−142.15	50.03	−4.40	1
Cyclohexanone + 1-butanol	−90.57	38.69	−18.11	1
Cyclohexanone + 1-pentanol	−65.03	27.71	−15.53	2
Cyclohexanone + 1-hexanol	−24.41	3.96	19.47	0

[a] In the case of the DMF + cyclohexanone system, k'_{s} are close to experimental error [13] and not included in the table.

3. Results and discussion

The ultrasonic sound velocity (u), density (ρ), isentropic compressibility (k_{s123}) and their related data for four ternary mixtures are presented in table 3. The Δk_{s123} have been fitted into smoothing equation.

$$\Delta k_{s123} = \phi_1 \phi_2 \phi_3[A + B\phi_1(\phi_2 - \phi_3) + C\phi_1^2(\phi_2 - \phi_3)^2] \quad (7)$$

Table 3. The values of density (ρ), sound velocity (u), isentropic compressibility (k_{s123}) and its related properties for the ternary mixtures of *N*,*N*-dimethylformamide (1) + cyclohexanone (2) + 1-alkanols (3) at 303.15 K.

				T Pa^{-1}			
ϕ_1	ϕ_3	ρ (g cm^{-3})	u (m s^{-1})	k_{s123}	k'_{s123}	$k''_{s123(b)}$	Δk_{s123}
DMF (1) + cyclohexanone (2) + 1-propanol (3)							
0.1214	0.7418	0.83322	1251	767	−29	−37	8
0.2259	0.6143	0.85155	1281	712	−31	−47	16
0.3011	0.5022	0.86761	1311	671	−34	−51	17
0.4096	0.4061	0.88129	1339	633	−34	−49	15
0.5221	0.2904	0.89800	1376	588	−34	−40	6
0.6009	0.1921	0.91194	1409	552	−32	−29	−3
0.7156	0.0900	0.92678	1428	529	−14	−13	−1
0.7897	0.0531	0.93235	1439	518	−9	−7	−2
0.8172	0.0634	0.93115	1440	518	−11	−9	−2
0.8888	0.0460	0.93408	1448	511	−8	−5	−3
DMF (1) + cyclohexanone (2) + 1-butanol (3)							
0.0857	0.7658	0.83392	1274	739	−21	−17	−7
0.2074	0.6285	0.85263	1304	690	−26	−22	−4
0.2623	0.6173	0.85431	1307	685	−24	−21	−3
0.2995	0.5102	0.86869	1331	650	−28	−23	−5
0.3649	0.4771	0.87347	1340	638	−27	−24	−3
0.4820	0.3369	0.89279	1377	591	−29	−21	−8
0.5782	0.2341	0.90710	1404	559	−27	−16	−11
0.7001	0.1134	0.92403	1429	530	−15	−8	−7
0.7589	0.0603	0.93139	1437	520	−7	−4	−3
0.8825	0.0517	0.93350	1446	512	−6	−3	−3
DMF (1) + cyclohexanone (2) + 1-pentanol (3)							
0.0722	0.8259	0.83008	1290	724	−14	−6	−8
0.1833	0.6735	0.84973	1318	677	−20	−4	−16
0.2455	0.6182	0.85695	1329	661	−20	−2	−18
0.2639	0.5455	0.86628	1353	631	−32	−3	−29
0.3618	0.5034	0.87207	1344	635	−13	−2	−15
0.4408	0.4135	0.88399	1369	604	−19	3	−22
0.5392	0.3051	0.89850	1401	567	−26	4	−30
0.6569	0.1937	0.91362	1426	538	−23	3	−26
0.7597	0.0984	0.92661	1435	524	−9	2	−11
0.8708	0.0611	0.93231	1442	516	−2	3	−5
DMF (1) + cyclohexanone (2) + 1-hexanol (3)							
0.0532	0.8805	0.82666	1303	712	−9	−3	−6
0.1097	0.7739	0.83979	1325	678	−19	−5	−14
0.1557	0.7154	0.84701	1336	661	−22	−5	−17
0.2175	0.6386	0.85657	1348	642	−23	−3	−20
0.3224	0.5357	0.86950	1360	622	−17	1	−18
0.4243	0.4424	0.88143	1373	602	−13	6	−19
0.5198	0.3655	0.89146	1382	587	−8	9	−17
0.6355	0.2413	0.90764	1417	549	−15	11	−26
0.7381	0.1214	0.92350	1443	520	−15	9	−24
0.8604	0.0675	0.93133	1445	514	−4	7	−11

Table 4. Values of parameters A, B, C and the standard deviation (σ) of ternary systems at 303.15 K.

	$T\,Pa^{-1}$			
	A	B	C	$\sigma(\Delta k_{s123})$
DMF (1) + cyclohexanone (2)				
+ 1-propanol (3)	−380	−4148	73,015	3
+ 1-butanol (3)	−661	−429	36,618	3
+ 1-pentanol (3)	−1301	2304	53,721	1
+ 1-hexanol (3)	−2215	−8403	23,708	2

The adjustable parameters A, B and C are obtained from the least-squares analysis and are given in table 4 along with standard deviation (σ).

A close examination of results included in table 3 shows that k'_{s123} values are negative at all volume fraction compositions studied in all four ternary mixtures. The results indicate that there is a much strong interaction in these liquid mixtures. Due to the polar nature of DMF, cyclohexanone and alcohols, the dipole–dipole interactions prevail in these mixtures. When the compounds are mixed, the changes that occur in association equilibria are evidently rupture of the hydrogen bonds in pure cyclohexanone and 1-alkanols and DMF–DMF dipole–dipole interactions, and the formation of O–H···C=O and perhaps even O–H···$N(CH_3)_2$ hydrogen bonds between the components. A similar type of behaviour should have been observed in another ternary system of DMF, and cyclopentanone with 1-alkanols [14]. On the other hand, the large negative k'_{s123} valves are observed in DMF, and methyl ethyl ketone with 1-alkanols [15] mixtures. This indicates that a radical difference between an aliphatic ketone and a cyclic ketone. However, the structural effects and a detailed evaluation of orientational effects are difficult to interpret in ternary mixtures [16,17].

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