Speed of Sound and Isentropic Compressibilities of *N,N*-Dimethylformamide + Methyl Isobutyl Ketone + 1-Alcohols at 303.15 K

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Speed of sound and densities were measured for *N,N*-dimethylformamide + methyl isobutyl ketone + 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol at 303.15 K. Isentropic compressibilities and excess isentropic compressibilities from ideality were computed. Excess isentropic compressibility values are negative throughout the range of volume fraction in all four ternary mixtures.

Introduction

The speed of sound and its related properties have been used to study physicochemical behavior and molecular interactions in a variety of liquid mixtures (Iloukhani and Rao 1985; Venkatesu et al. 1993). A survey of the literature reveals that no one has studied the isentropic compressibilities for the ternary systems of *N,N*-dimethylformamide + methyl isobutyl ketone + 1-alcohols, namely, 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol. This study is very important because of their extensive use in the textile industry, the leather industry, the pharmaceutical industry, and in many others. The present study was undertaken to compute the isentropic compressibility from speed-of-sound measurements and density evaluated from excess volumes. Here we present results for the isentropic compressibilities of *N,N*-dimethylformamide + methyl isobutyl ketone with 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol at 303.15 K.

Experimental Section

Apparatus and Procedure. Isentropic compressibilities were computed from the measured speed of sound, and the densities evaluated from excess volumes. The speed of sound was measured by a single-crystal ultrasonic interferometer at 4 MHz frequency at 303.15 K. These were accurate to 0.02%. The temperature was maintained by circulating water around a liquid cell from a thermostat controlled at (303.15 ± 0.01) K. Densities of pure compounds were determined with a bicapillary type pycnometer, which offers an accuracy of 2 parts in 10^5. The measured densities and those reported in the literature are listed in Table 1.

Materials. All the chemicals used were analytical grade. *N,N*-Dimethylformamide was purified as described previously (Venkatesu et al. 1994). Methyl isobutyl ketone was dried over potassium carbonate for 3 days and then fractionally distilled (Venkatesu and Rao 1994). The 1-alkanols were further purified by the methods described by Rao and Naidu (1974). The purities of the samples were checked by comparing the measured densities of the compounds with those reported in the literature (Riddick and Bunger, 1970; Timmermans, 1950). The purities of the samples were further confirmed by GLC single sharp peaks.

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Table 1. Densities (ϱ) of Pure Components at 303.15 K

component	ϱ/g cm^{-3} exptl	ϱ/g cm^{-3} lit. (1970; 1950)
N,N-dimethylformamide	0.941 18	0.941 20
methyl isobutyl ketone	0.796 07[a]	0.796 10[a]
1-propanol	0.796 01	0.796 00
1-butanol	0.802 03	0.802 06
1-pentanol	0.807 61	0.807 64
1-hexanol	0.812 03	0.812 01

[a] At 298.15 K.

Table 2. Volume Fraction of *N,N*-Dimethylformamide, ϱ, U, K_s, and K_s^E for *N,N*-Dimethylformamide (1) + Methyl Isobutyl Ketone (2) at 303.15 K

ϕ_1	ϱ/g cm^{-3}	U_{exp}/m s^{-1}	K_s/T Pa^{-1}	K_s^E (12)/T Pa^{-1}
0.1016	0.807 47	1203	856	−24
0.1823	0.820 15	1225	813	−32
0.2130	0.824 91	1235	795	−37
0.3163	0.840 82	1264	744	−44
0.4127	0.855 46	1291	701	−46
0.5504	0.876 15	1331	645	−45
0.6620	0.892 69	1365	601	−40
0.8319	0.917 42	1415	544	−25
0.8949	0.926 41	1436	523	−19

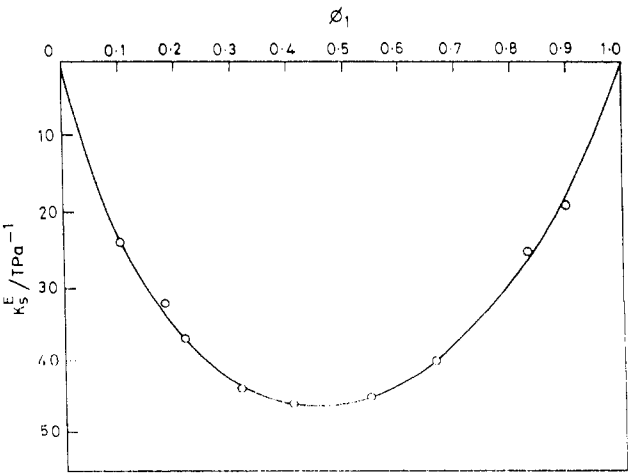

Figure 1. Excess isentropic compressibility (K_s) plotted against the volume fraction of *N,N*-dimethylformamide with methyl isobutyl ketone at 303.15 K.

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Table 3. Values of Parameters b_0, b_1, b_2, and the Standard Deviation (T Pa^{-1}) $\sigma(K_s^E)$ for Binary Systems at 303.15 K

system	b_0	b_1	b_2	$\sigma(K_s^E)$
N,*N*-dimethylformamide + methyl isobutyl ketone	−179.9	34.4	−70.5	1
N,*N*-dimethylformamide + 1-propanol	−225.6	35.6	89.5	2
N,*N*-dimethylformamide + 1-butanol	−92.3	−16.5	69.1	1
N,*N*-dimethylformamide + 1-pentanol	37.2	8.8	−5.9	1
N,*N*-dimethylformamide + 1-hexanol	37.6	107.4	−2.8	1
methyl isobutyl ketone + 1-propanol	−4.37	−33.62	−4.19	1
methyl isobutyl ketone + 1-butanol	−31.36	3.48	10.06	1
methyl isobutyl ketone + 1-pentanol	−24.31	−28.89	−28.45	0
methyl isobutyl ketone + 1-hexanol	−32.19	−28.68	−3.09	0.4

Table 4. Experimental Values for Isentropic Compressibilities of Ternary Mixtures: *N*,*N*-Dimethylformamide (1) + Methyl Isobutyl Ketone (2) + 1-Alkanols (3) at 303.15 K

ϕ_1	ϕ_3	ϱ/g cm^{-3}	U_{exp}/m s^{-1}	K_s/T Pa^{-1}	$K_s^E(123)$/T Pa^{-1}	$K_s^{E'}(123)$/T Pa^{-1}	$dK_s^E(123)$/T Pa^{-1}
			N,*N*-Dimethylformamide (1) + Methyl Isobutyl Ketone (2) + 1-Propanol (3)				
0.0950	0.7322	0.809 46	1210	844	−14	−16	2
0.1700	0.6366	0.820 54	1232	803	−26	−29	3
0.2626	0.6084	0.834 24	1258	757	−33	−41	8
0.3028	0.5211	0.840 11	1268	740	−36	−44	8
0.3843	0.4482	0.852 06	1292	703	−41	−50	9
0.4804	0.3364	0.866 27	1318	665	−42	−50	8
0.5701	0.2759	0.879 42	1342	631	−40	−49	9
0.6079	0.1861	0.884 91	1352	618	−40	−44	4
0.7268	0.1232	0.902 18	1388	575	−34	−35	1
			N,*N*-Dimethylformamide (1) + Methyl Isobutyl Ketone (2) + 1-Butanol (3)				
0.0916	0.7561	0.813 36	1240	800	−14	−10	−4
0.1285	0.6673	0.818 02	1249	782	−22	−14	−8
0.1869	0.6516	0.826 53	1262	760	−23	−16	−7
0.2923	0.5421	0.841 27	1286	719	−31	−25	−6
0.3448	0.4788	0.848 57	1300	697	−35	−29	−6
0.4655	0.3443	0.865 59	1332	651	−42	−33	−9
0.5570	0.2751	0.878 75	1355	620	−40	−32	−8
0.6621	0.1813	0.893 91	1378	589	−35	−30	−5
0.7741	0.0829	0.909 90	1405	557	−29	−27	−2
			N,*N*-Dimethylformamide (1) + Methyl Isobutyl Ketone (2) + 1-Pentanol (3)				
0.0716	0.7547	0.814 36	1259	775	−11	−2	−9
0.1631	0.6737	0.826 47	1280	739	−20	−4	−16
0.1959	0.6597	0.831 06	1286	728	−19	−3	−16
0.2914	0.5430	0.843 55	1306	695	−27	−6	−21
0.3614	0.4579	0.852 75	1319	674	−30	−7	−23
0.4561	0.3637	0.865 68	1341	642	−35	−9	−26
0.5359	0.2945	0.876 77	1360	617	−36	−11	−25
0.6694	0.1695	0.895 52	1383	584	−30	−15	−15
0.7960	0.0959	0.913 15	1411	550	−20	−13	−7
			N,*N*-Dimethylformamide (1) + Methyl Isobutyl Ketone (2) + 1-Hexanol (3)				
0.0537	0.7911	0.815 69	1278	751	−10	−6	−4
0.1051	0.7354	0.822 12	1285	737	−12	−7	−5
0.1801	0.6851	0.832 10	1300	711	−15	−8	−7
0.2651	0.5624	0.842 29	1308	694	−17	−9	−8
0.3498	0.4640	0.852 97	1318	675	−17	−9	−8
0.4398	0.3693	0.864 64	1331	653	−18	−10	−8
0.5394	0.2859	0.877 90	1348	627	−16	−8	−8
0.6174	0.2376	0.888 57	1364	605	−13	−6	−7
0.6882	0.1774	0.898 10	1380	585	−14	−7	−7
0.8085	0.0943	0.914 67	1408	551	−11	−6	−5

Results and Discussion

The Isentropic compressibility (K_s) of the ternary mixtures was calculated from the expression

$$K_s = U^{-2}\varrho^{-1} \tag{1}$$

The density of the ternary mixtures was computed using the relation

$$\varrho = \frac{x_1M_1 + x_2M_2 + x_3M_3}{V \pm V^E} \tag{2}$$

where U and ϱ denote the speed of sound and density, respectively, of the mixture. 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 above mixtures have already been published (Venkatesu and Rao 1994).

The excess isentropic compressibility, $K_s^E(123)$ was calculated using the relation

$$K_s^E(123) = K_s(123) - \phi_1K_s(1) - \phi_2K_s(2) - \phi_3K_s(3) \tag{3}$$

where ϕ_1, ϕ_2, ϕ_3, and $K_s(1)$, $K_s(2)$, and $K_s(3)$ are volume fractions and isentropic compressibilities of the three pure components.

$dK_s^E(123)$, the difference between the measured value of $K_s^E(123)$ and that of computed from binary data $K_s^{E'}(123)$, have been calculated using the relation

$$dK_s^E(123) = K_s^E(123) - K_s^{E'}(123) \tag{4}$$

Table 5. Values of Parameters *A*, *B*, and *C* and the Standard Deviation (T Pa^{-1}) $\sigma[dK_s^E(123)]$ of Ternary Mixtures at 303.15 K

system	*A*	*B*	*C*	$\sigma[dK_s^E(123)]$
N,*N*-dimethylformamide + methyl isobutyl ketone + 1-propanol	136	−1103	5667	2
N,*N*-dimethylformamide + methyl isobutyl ketone + 1-butanol	−321	1437	18735	2
N,*N*-dimethylformamide + methyl isobutyl ketone + 1-pentanol	−846	4477	46930	1
N,*N*-dimethylformamide + methyl isobutyl ketone + 1-hexanol	−691	−8903	−52081	2

The latter quantity was computed using the relation

$$K_s^{E'}(123) = K_s^E(12) + K_s^E(13) + K_s^E(23) \quad (5)$$

where $K_s^E(12)$, $K_s^E(13)$, and $K_s^E(23)$ denote excess isentropic compressibilities for the three binary mixtures, and these are estimated using the smoothing equation

$$K_s^E(ij) = \phi_i\phi_j[b_0 + b_1(\phi_i - \phi_j) + b_2(\phi_i - \phi_j)^2] \quad (6)$$

where b_0, b_1, and b_2 are constants obtained by the methods of least squares.

The binary parameters of excess isentropic compressibility for the mixtures of *N*,*N*-dimethylformamide with 1-alcohols (Rao and Reddy, 1985) and methyl isobutyl ketone with 1-alcohols (Reddy and Naidu, 1979) were taken from literature. The excess isentropic compressibilities for the binary mixture *N*,*N*-dimethylformamide + methyl isobutyl ketone at 303.15 K have been measured in the present investigations. K_s^E for this binary system exhibits negative deviation from ideal behavior of the entire range of the composition. The data are presented in Table 2 and graphically represented in Figure 1. The negative deviation indicates that the structure-making effect is dominant in the mixture. These parameters for all the binary systems are presented in Table 3. The experimental data for four ternary mixtures are listed in Table 4.

The $dK_s^E(123)$ have been fitted into the smoothing equation

$$dK_s^E(123) = \phi_1\phi_2\phi_3[A + B\phi_1(\phi_2 - \phi_3) + C\phi^2{}_1(\phi_2 - \phi_3)^2] \quad (7)$$

where ϕ_1, ϕ_2, and ϕ_3 are the volume fractions of components 1, 2, and 3, respectively. *A*, *B*, and *C* are adjustable parameters, and these parameters are evaluated by the method of least squares and are given in Table 5 along with standard deviation, $\sigma[dK_s^E(123)]$.

$K_s^E(123)$ values are negative throughout the range of volume fraction in all four ternary mixtures. The negative deviation is an indication of strong interactions in the liquid mixtures. It is attributed to charge-transfer, dipole–induced dipole and dipole–dipole interactions, which leads to a decrease in free length and increase in sound velocity. A positive sign indicates weak interactions and is attributed to dispersion forces. The experimental results suggest that the former effect is dominant in all four ternary mixtures.

The results indicate that there is a much stronger interaction between the compounds. Due to the high polar nature of DMF, which may induce polarity in methyl isobutyl ketone and 1-alkanols, there may be an induced dipole–dipole interaction. When the compounds are mixed, the changes that occur in association equilibria are evidently rupture of the hydrogen bonds in pure compounds and the formation of O—H···C=O hydrogen bonds between the components. The abnormal behavior of these compounds may be thought of as being due to a resonance structure in these compounds.

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