DENSITY AND SPEED OF SOUND OF BINARY MIXTURES OF SOME ALIPHATIC ESTERS WITH N-METHYLACETAMIDE AT 308.15 K

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ABSTRACT

The densities and sound speeds of mixtures of methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate with N-methylacetamide, over the entire range of composition, have been measured at 308.15 K. The deviations in isentropic compressibility $\Delta\kappa_s$ have been computed using speed and density values. The results are discussed in the light of intermolecular interactions occurring in the solutions. The computed results of $\Delta\kappa_s$ have been fitted to a Redlich-Kister type polynomial equation.

Keywords: *Binary mixtures; N-methylacetamide; alkyl esters; deviation in isentropic compressibility.*

INTRODUCTION

Solvent structure determines the nature of interactions between the like and unlike molecules of a liquid binary mixture. It also provides basic information to use in evaluating the solute-solvent interactions. N-methylacetamide is an important solvent possessing strong hydrogen bonds and protic and basic character. Esters, find applications such as plasticizers in polymer-processing industries in order to impart favorable thermoplastic behavior and also in the flavor and fragrance industries. N-methylacetamide is chosen as a solvent because of its solvent properties, have been the subject of considerable interest due to the versatility as a solvent and its close relationship peptides and proteins. A survey of the literature indicates that no acoustical data on these mixtures has been produced. This prompted us to understand a study on the speed of sound at a temperature 308.15 K.

EXPERIMENTAL

Materials:

All the esters methyl acetate (99.5 %), ethyl acetate (99.8 %), n-propyl acetate (99.5 %) and n-butyl acetate (≥99 %) were made of Sigma-Aldrich, USA are stored over molecular sieves (0.3 nm Merck, India). The high purity grade N-methylacetamide (99.9 %) is also furnished by Sigma-Aldrich chemicals, USA and was used without further purification. Densities and speed of sound of pure substances and their comparison with literature values are listed Table 1.

Apparatus and procedure:

Binary mixtures were prepared by mass in air tight bottles. The mass measurements were performed on a Dhona 100 DS, India, single pan analytical balance with a resolution of ± $0.01 \cdot 10^{-6}$ kg. The required properties of the mixture were measured on the same day. The possible error in mole fraction was estimated to be less than ± $1 \cdot 10^{-4}$.

Density of pure liquids and their mixtures were determined by using a $1 \cdot 10^{-5}$ m^3 double arm pycnometer [1]. The density values from triplicate replication at the temperature of 308.15 K were reproducible within ± $2 \cdot 10^{-2}$ $kg \cdot m^{-3}$. The uncertainty in density values was found to be ± 0.04 $kg \cdot m^{-3}$.

Speed of sound values were measured by using a single-crystal variable-path interferometer (Mittal Enterprises, India) operating at 2 MHz frequency which was calibrated with water and benzene. The detailed procedure was described in our previous papers[2,3]. The uncertainty in speed of sound and deviation in isentropic compressibility was found to be 0.2 %.

In all the property measurements the temperature was controlled within ± 0.01 K using a constant temperature bath (INSREF model IRI – 016 C, India) by circulating water from the thermostat.

RESULTS AND DISCUSSION

Experimental values of densities (ρ) and speed of sound (u) for the binary mixtures of N-methylacetamide with methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate at 308.15 K are listed as a function of volume fraction in Table 2.

The density values have been used to calculate excess molar volumes (V^E) using the following equation;

$$V^E/(m^3 \cdot mol^{-1}) = (x_1M_1 + x_2M_2) / \rho_m - (x_1M_1/ \rho_1 + x_2M_2/ \rho_2) \quad (1)$$

where ρ_m is the density of the mixture; x_1, M_1, ρ_1 and x_2, M_2 and ρ_2 are the mole fraction, molecular weight and density of pure components respectively.

The speed of sound (u) was used to calculate the isentropic compressibility (κ_s) using the equation

$$\kappa_s = 1/ u^2 \rho \quad (2)$$

The excess isentropic compressibility (Δk_s) has been evaluated using the equation

$$\Delta k_s/(m^2 \cdot N^{-1}) = \kappa_S - (\Phi_1 \kappa_{S1} + \Phi_2 \kappa_{S2}) \quad (3)$$

where κ_{S1}, κ_{S2} and κ_S are the isentropic compressibility of the pure components and observed isentropic compressibility of liquid mixture respectively.

Φ_1 is the volume fraction and is calculated from the individual pure molar volumes, V_i, with the relation

$$\Phi_1 = x_i V_i/(\Sigma x_i V_i) \quad (4)$$

The excess or deviation properties Y^E were fitted by the method of non linear least squares to a Redlich-Kister type polynomial[4-9].

$$Y^E = x_1x_2 \Sigma A_i (x_1-x_2)^i \quad (5)$$

In each case, the optimum number of coefficients A_i was determined from an examination of the variation of standard deviation (σ) as calculated by

$$\sigma (Y^E) = [\Sigma (Y^E_{obs} - Y^E_{cal}) / (n - m)]^{1/2} \quad (6)$$

where 'n' represents the number of experimental points and 'm' is the number of coefficients. It is found that for the solution of the fifth degree polynomial, the agreement between the experimental values and the calculated ones is satisfactory. The derived parameters (A_i) and the estimated standard deviation (σ) for V^E and $\Delta\kappa_s$ are given in Table 3.

Excess molar volumes of N-methylacetamide + esters at 308.15 K are displayed in figure 1. The values of V^E are negative for all the mixtures of N-methylacetamide +methyl acetate, +ethyl acetate, +propyl acetate and +butyl acetate over the whole mole fraction range and show a increasing tendency with increasing chain length of the ester molecules. The negative values of V^E vary in the algebraic order:

MA > EA > PA > BA

The maximum interactions are exhibited by all the esters around the mole fraction $x_1 = 0.5$. The negative excess molar volumes increase with increase in the chain length of the ester which

implies that butyl acetate has maximum interaction, while methyl acetate has minimum interaction.

Esters (methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate) are weak hydrogen accept acceptors and they are not donors due to the lack of an acidic proton. In these mixtures the observed negative values of V^E are attributed to the combined effect of specific interactions and free volume is outweighed the dispersion interactions. The graphical evidence supports the above said forces are operating between the unlike molecules of NMA and esters.

N-methylacetamide is strongly associated liquid, when it is mixed with esters it looses its aggregates contributing to the expansion of volume, hence declustering of NMA molecules. From the isothermal curves at 308.15 K shown in the figure 1, it is clear that in case of esters with NMA the volume reduction factors are preponderant.

The curves in figure 2 show that $\Delta\kappa_s$ values are negative over the entire volume fraction of (NMA (Φ_l) + MA, NMA (Φ_l) + EA, NMA (Φ_l) + PA and NMA (Φ_l) + BA). The values of $\Delta\kappa_s$ may be attributed to the chemical forces operating between the unlike molecules, also these values decrease systematically with increasing size of the ester molecules. The interaction order of $\Delta\kappa_s$ is in algebraic order:

$$MA > EA > PA > BA$$

The values of $\Delta\kappa_s$ decrease with increase in chain length of ester. The order indicates that the mixtures are more compressible than the corresponding ideal mixtures. Due to this the speed of sound increases and the compressibility decreases until the maxima are reached. In the present investigation the factors responsible for negative deviation in isentropic compressibility are dominant.

Usually the behavior of V^E and $\Delta\kappa_s$ are similar in nature. This tendency is also found in the present systems, showing the same sign and order. Thus, the sign of $\Delta\kappa_s$ supports the postulates used to interpret the sign of excess molar volume.

CONCLUSIONS

Densities and speed of sound for binary mixtures consisting of N-methylacetamide with methyl acetate, ethyl acetate, propyl acetate and butyl acetate have been measured at 308.15 K. The corresponding excess molar volumes and excess isentropic compressibility have been calculated and correlated using the Redlich-Kister polynomial equation. The derived values have been discussed.

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Table 1. Experimental densities (ρ) and speed of sound (u) of pure components at 308.15 K.

Component	$10^{-3}\cdot\rho$ / (kg·m^{-3})		u / (m·s^{-1})	
	Expt	Lit	Expt	Lit
N-Methylacetamide (1)	0.94591	0.9460[5]	1362.0	1360[6]
Methyl acetate (2)	0.91242	0.91522[7]	1112.1	
Ethyl acetate (2)	0.88260	0.88250[8]	1097.8	1095[8]
n-Propyl acetate (2)	0.87305	0.8718[9]	1139	
n-Butyl acetate (2)	0.86711	0.8655[9]	1155.3	

Table 2. The values of density (ρ), speed of sound (u), excess molar volume (V^E), and deviation in isentropic compressibility ($\Delta\kappa_s$) of the binary mixtures of N-methylacetamide (1) + aliphatic ester (2) at T = (308.15) K

Φ_1	$10^{-3}\cdot\rho$ (kg · m^{-3})	u (m · s^{-1})	$10^6 \cdot V^E$ (m^3 · mol^{-1})	$10^{11} \cdot \Delta\kappa_s$ (m^2 · N^{-1})
N-methylacetamide (1) + methyl acetate (2)				
0.0000	0.9124	1112.1	0.0000	0.0000
0.0226	0.9142	1121.1	-0.0908	-0.8727
0.1461	0.9195	1150.5	-0.1944	-1.8359
0.2707	0.9244	1179.2	-0.2527	-2.2444
0.3964	0.9288	1208.6	-0.2698	-2.3759
0.4998	0.9323	1233.7	-0.2672	-2.3328
0.6047	0.9356	1260.4	-0.2470	-2.2104
0.7323	0.9394	1294.1	-0.2052	-1.8990
0.8544	0.9427	1326.7	-0.1381	-1.3263
0.9799	0.9457	1358.8	-0.0385	-0.3533
1.0000	0.9459	1362.0	0.0000	0.0000

N-methylacetamide (1) + ethyl acetate (2)				
0.0000	0.8826	1097.8	0.0000	0.0000
0.0537	0.8875	1113.5	-0.1663	-1.1490
0.1841	0.8969	1148.6	-0.2796	-2.6860
0.2969	0.9046	1179.5	-0.3255	-3.5609
0.3988	0.9114	1207.5	-0.3489	-3.9968
0.4979	0.9179	1234.4	-0.3594	-4.0827
0.5937	0.9239	1258.8	-0.3426	-3.7272
0.6952	0.9300	1284.3	-0.3030	-3.0856
0.7434	0.9328	1296.2	-0.2761	-2.6819
0.9463	0.9439	1347.8	-0.1161	-0.6588
1.0000	0.9459	1362.0	0.0000	0.0000
N-methylacetamide (1) + n-propyl acetate (2)				
0.0000	0.8731	1139.0	0.0000	0.0000
0.0246	0.8761	1162.0	-0.1657	-2.9854
0.1391	0.8873	1193.0	-0.5066	-4.7507
0.2709	0.8991	1224.3	-0.7212	-5.6091
0.3828	0.9083	1250.4	-0.7925	-5.8928
0.4974	0.9172	1275.5	-0.8041	-5.7070
0.5910	0.9235	1295.2	-0.7188	-5.2023
0.6784	0.9286	1311.3	-0.5728	-4.4031
0.7634	0.9333	1325.5	-0.4171	-3.4102
0.9797	0.9453	1356.6	-0.0723	-0.1442
1.0000	0.9459	1362.0	0.0000	0.0000
N-methylacetamide (1) + n-butyl acetate (2)				
0.0000	0.8671	1155.3	0.0000	0.0000
0.0220	0.8705	1162.5	-0.2511	-0.7528
0.1461	0.8862	1207.1	-1.0345	-4.6635
0.2680	0.8999	1246.5	-1.4521	-7.0021
0.3961	0.9120	1276.2	-1.5570	-7.4297
0.4973	0.9205	1294.2	-1.5148	-6.9169
0.6045	0.9276	1313.5	-1.2869	-6.1387
0.7304	0.9350	1334.5	-0.9644	-4.8637
0.7866	0.9380	1343.1	-0.8071	-4.1678
0.8544	0.9409	1351.5	-0.5664	-3.0863
1.0000	0.9459	1362.0	0.0000	0.0000

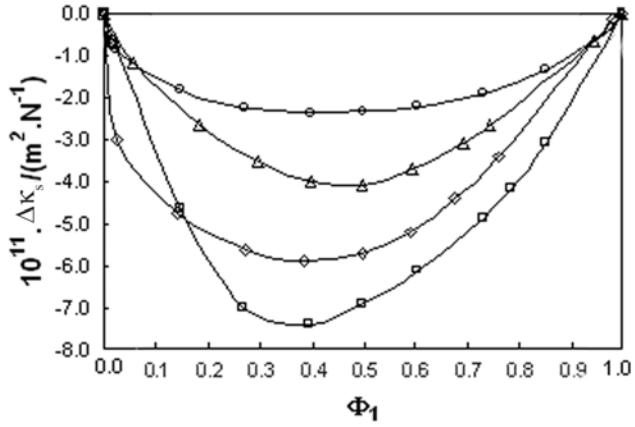

Fig.-1: Plots of deviation in isentropic compressibility, $\Delta\kappa_s/(m^2 \cdot N^{-1})$ against volume fraction (Φ_1) ofNMA for {(Φ_1) NMA +(Φ_2) MA (○), +(Φ_2) EA (Δ), +(Φ_2) PA (◊) and +(Φ_2) BA (□)} at T = 308.15 K.

Table 3. Binary coefficients (A_i) and Standard deviations (σ) for the binary mixtures at T/K=308.15

Binary system	Function	A_0	A_1	A_2	A_3	A_4	σ
N-methylacetamide (1) +	$V^E \cdot 10^6/(m^3 \cdot mol^{-1})$	-1.1446	-0.1979	1.1798	1.2953	-3.4838	0.1472
Methyl acetate (2)	$\Delta\kappa s \cdot 10^{11}/(m^2 \cdot N^{-1})$	-10.0642	-2.9623	9.6556	15.2996	-32.6656	1.5859
Ethyl acetate (2)	$V^E \cdot 10^6/(m^3 \cdot mol^{-1})$	-1.4414	-0.1108	0.0573	0.1791	-2.1563	0.0282
	$\Delta\kappa s \cdot 10^{11}/(m^2 \cdot N^{-1})$	-16.3043	2.3940	5.3236	3.7310	-8.9954	0.1733
Propyl acetate (2)	$V^E \cdot 10^6/(m^3 \cdot mol^{-1})$	-3.3648	-0.0105	2.4363	-0.0598	-4.7411	0.2145
	$\Delta\kappa s \cdot 10^{11}/(m^2 \cdot N^{-1})$	-25.7334	-12.2619	51.8929	79.8975	-104.8585	6.9893
Butyl acetate (2)	$V^E \cdot 10^6/(m^3 \cdot mol^{-1})$	-6.2696	-0.8639	0.7034	0.7627	-2.0215	0.0857
	$\Delta\kappa s \cdot 10^{11}/(m^2 \cdot N^{-1})$	-27.7943	13.3109	-12.9106	-8.5274	11.9168	0.2574

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