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Acoustical studies on intermolecular interactions in binary liquid mixtures of N,N-dimethylacetamide with acetone and acetonitrile at 298.15K

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ABSTRACT

The measurements of ultrasonic velocities (υ), densities (ρ) and viscosities (η) of binary liquid mixtures of N-N-dimethylacetamide with acetone and acetonitrile have been carried out over the entire range of composition at temperature 298.15 K. Measured values are used to evaluated the other thermo dynamical parameters such as adiabatic compressibility (β_α), free length (L_f), free volume (V_f) with their excess values as β_α^E, L_f^E and V_f^E. From the properties of these excess parameters the nature and strength of the interactions in these binary systems are discussed. The non linearity found in all the plots of these ultrasonic parameters and their excess values for the composition range indicates presence of the intermolecular interaction between the components of the unlike molecules of the mixture.

Keywords: Ultrasonic velocity, excess values, compressibility, free volume, molecular interaction.

INTRODUCTION

For determining the molecular structure & molecular properties of different materials there are many physical methods. The advances in recent years in the ultrasonic technique have become a powerful tool in evaluating information about the physical and chemical behaviour of molecules of the liquids[1-4]. The ultrasonic studies of the liquids are most preferred in many fields such as pharmaceutical industry, biomedical research, automobile industry, chemical industry, water research & scattering spectroscopy, etc.[5] The information of density (ρ), ultrasonic velocity (υ) and viscosity (η) of the pure liquids and their mixtures have been widely used in the field of interactions and structural aspect evaluation studies

In the present study the ultrasonic velocity , density and viscosity measurements have been carried out for different concentrations at temperature 298.15K of the pure liquids and its mixtures to determine various ultrasonic parameters such as compressibility (β_α), free length (L_f) and free volume (V_f) and their excess values, excess adiabatic compressibility (β_α^E), excess free length (L_f^E), excess free volume (V_f^E) for the different composition range of NN-Dimethylacetamide (NNDMA) in acetone and acetonitrile at temperatures 298.15K. The variations of these parameters with concentration of binary liquid mixtures are studied to understand molecular interactions between unlike components of the mixtures.

MATERIALS AND METHODS

The chemicals NN-dimethylacetamide is from Qualigens and having excel grade (99.5%) purity, acetone and acetonitrile are from Merck specialities Pvt. Limited and are of GR grade (99%) purity, all the liquids are used without further purification. The binary mixtures for different range of composition were prepared at room

temperature and kept in a special airtight glass bottles to avoid air contact. The mixtures were used within 24 hours of its preparation. The ultrasonic interferometer (Mittal enterprises, New Delhi, India) is a single and direct device to determine ultrasonic velocity in liquids with a high degree of accuracy[6]. Here the measurements of ultrasonic velocities were carried out on single crystal multi frequency ultrasonic interferometer operating at 1MHz (M-81). The constant temperature of the liquid inside the interferometer cell was maintained by circulating water through the outer jacket by electronically controlled thermostat. Accuracy in the measurement of ultrasonic velocity was within ±0.01m/s and the temperature of the test liquids during measurement were maintained within an accuracy of $\pm 0.1^0$C. The densities of the binary mixtures & pure liquids were measured using 25ml specific gravity bottle and a sensitive mono pan balance (K-Roy, K-12 classic) within ±0.1mg accuracy. The viscosity of the liquids and their mixtures were measured using the suspended level viscometer.

The experimentally measured ultrasonic velocity (υ) measured in ms^{-1}, density (ρ) in kgm^{-3} and viscosity (η) in Nsm^{-2} are used to evaluate various thermo dynamical parameters like—

(1) Adiabatic compressibility (β_α) by the relation,

$$\beta_\alpha = 1/\upsilon^2\rho \qquad \text{----------1}$$

(2) Intermolecular free length (L_f) by the relation,

$$L_f = K\beta_\alpha^{1/2} \qquad \text{---------- 2}$$

Where, K is Jacobsons constant ($K=93.875 + 0.375\ T$) X 10^{-8} and T being the absolute temperature[7]

(3) The free volume by the relation,

$$V_f = \left[\frac{M_{eff}}{k\eta}\nu\right]^{3/2} \qquad \text{----------3}$$

Where, M_{eff} is the effective molecular weight
($M_{eff} = \Sigma m_i X_i$ in which m_i and X_i are the molecular weight and mole fraction of the individual constituents respectively), k is temperature independent constant which is equal to 4.28 X 10^9 for all liquids and

(4) The excess values are determined by using the relation

$$A^E = A_{exp} - A_{id} \qquad \text{----------4}$$

Where, A^E - excess parameters of all acoustic parameters,

$A_{id} = \sum_{i=1}^{n} A_i X_i$, A_i is any acoustical parameter and X_i – the mole fraction of liquid component.

RESULTS AND DISCUSSION

Experimentally determined values of ultrasonic velocity (υ), density (ρ), viscosity (η) and, adiabatic compressibility (β_α),free length (L_f), and free volume (V_f) has been evaluated and are reported in Table-1. The excess values of excess adiabatic compressibility (β_α^E), excess free length (L_f^E), excess free volume (V_f^E) for N,N-dimethylacetamide +acetone, acetonitrile at 298.15K are reported in Table-2

From Table-1 and figures-1, it is observed that ultrasonic velocity (υ), density (ρ) and viscosity (η) increases with increase in the mole fraction of NNDMA in the binary mixture for both the systems studied.

As observed from the Table 1 and figure 1(C), the values of viscosity increase with the increasing concentration of NNDMA in NNDMA+Acetone and NNDMA+Acetonitrile binary mixtures systems. The compressibility values shows decreasing trend with the increasing concentration of NNDMA in acetone and acetonitrile mixtures.

Table 1. Ultrasonic velocity (υ), density (ρ) , viscosity (η) , adiabatic compressibility (β_α),free length (L_f), and free volume (V_f) for N,N-dimethylacetamide +acetone, acetonitrile at 298.15K.

Mole fractio of NNDMA	Velocity υ ms^{-1}	Density ρ kgm^{-3}	Viscosiy η μ Pas	Compessibilit β_α X 10^{-10} m^2N^{-1}	Free length L_f X10^{-8} m	Free Volume V_f X10^{-17} m^3/mol
N,N-dimethylacetamide + Acetone						
0.0000	1173.756	785.8768	317.4357	9.2361	6.2491	3.5543
0.1018	1205.282	806.1939	354.563	8.5385	6.0085	3.3756
0.2092	1243.579	828.628	401.5061	7.8036	5.7441	3.1638
0.3226	1278.000	848.8029	461.4371	7.2133	5.5226	2.8836
0.4425	1318.229	868.0338	526.1830	6.6295	5.2944	2.6752
0.5695	1357.294	888.5246	603.2867	6.1092	5.0824	2.4567
0.7043	1393.471	905.757	711.8773	5.6858	4.9031	2.1524
0.8475	1429.313	922.3654	831.1138	5.3069	4.7369	1.9152
1.0000	1460.303	935.735	958.5252	5.0114	4.6032	1.7269
N,N-dimethylacetamide + Acetonitrile						
0.0000	1277.777	777.0927	350.4041	7.8816	5.7728	2.0684
0.0750	1295.555	798.9739	389.847	7.4568	5.6150	2.0310
0.1591	1315.555	815.5309	430.5449	7.0850	5.4733	2.0299
0.2540	1335.555	838.6443	482.5791	6.6849	5.3165	1.9921
0.3620	1355.675	860.5452	554.5765	6.3229	5.1705	1.8933
0.4860	1375.555	878.6307	635.1884	6.0150	5.0431	1.8186
0.6300	1409.143	901.3729	743.2010	5.5871	4.8604	1.7294
0.7989	1440.952	922.1639	848.2380	5.2227	4.6992	1.7176
1.0000	1460.303	935.735	958.5252	5.0114	4.6032	2.0684

Table 2. Excess adiabatic compressibility (β_α^E), excess free length (L_f^E), excess free volume (V_f^E) for N,N- dimethylacetamide +acetone, acetonitrile at 298.15K

Mole fraction of NNDMA	Excess compressibility β_α^E X10^{-10} m^2N^{-1}	Excess free length L_f^EX 10^{-8} m	Excess free Volume V_f^EX10^{-17} m^3/mole
N,N-dimethylacetamide + Acetone			
0.0000	0.0000	0.0000	0.0000
0.1018	-0.26731	-0.07298	0.00737
0.2092	-0.54860	-0.16064	-0.00822
0.3226	-0.65990	-0.19555	-0.08117
0.4425	-0.73708	-0.22636	-0.07043
0.5695	-0.72090	-0.22935	-0.05693
0.7043	-0.57501	-0.18683	-0.11492
0.8475	-0.34885	-0.11728	-0.09042
1.0000	0.00000	0.00000	0.00000
N,N-dimethylacetamide + Acetonitrile			
0.0000	0.00000	0.00000	0.00000
0.0750	-0.209588	-0.070026	-0.01176
0.1591	-0.340117	-0.113481	0.01579
0.2540	-0.467738	-0.159233	0.01042
0.3620	-0.519763	-0.178871	-0.05144
0.4860	-0.471606	-0.161242	-0.08380
0.6300	-0.486536	-0.175646	-0.12385
0.7989	-0.366068	-0.139237	-0.07801
1.0000	0.00000	0.00000	0.00000

The same nature as that of compressibility is also observed in the free length and in the free volume.The increase in ultrasonic velocity with concentration may be attributed to the cohesion. The increase in density with concentration suggest a solute-solvent interaction exist between the NNDMA in acetone and acetonitrile mixtures. In other words the increase in density may be interpreted to the structure making of the solvent due to hydrogen bonding. The viscosity is an important parameter in understanding the structural as well as the molecular interaction occurring in the liquid mixtures. Here the values of viscosities are increasing with concentration. These variations attributed to structural changes[7].

The values of adiabatic compressibility (β_α) and free length (L_f) decreases with increase in the mole fraction of N-N dymethylacetamide. This suggests making and breaking of hydrogen bonding. The greater the attractive force among the molecules, the smaller will be the compressibility thus indicates formation of a complex[8]. The intermolecular free length depends upon intermolecular attractive and repulsive force. Eyring & Kincaid have proposed that free length is a predominating factor in determining the variation of ultrasonic velocity of solutions[9-10].

The decrease in adiabatic compressibility suggests that there is significant interaction exsists between unlike molecules of the mixture. The free length and free volume values shows decreasing trends with increase in the concentration of NNDMA in both the systems. Hence it can be concluded that there is significant interaction between the two liquids due to which the structural arrangement is also affected[11].

Figers 1. 1(A) Ultrasonic velocity (υ), 1(B) density (ρ) , 1(C) viscosity (η) and 1(D) excess adiabatic compressibility (β_α^E), 1(E) excess free length (L_f^E), 1(F) excess free volume (V_f^E) for N,N- dimethylacetamide +acetone and N,N- dimethylacetamide + acetonitrile at 298.15K

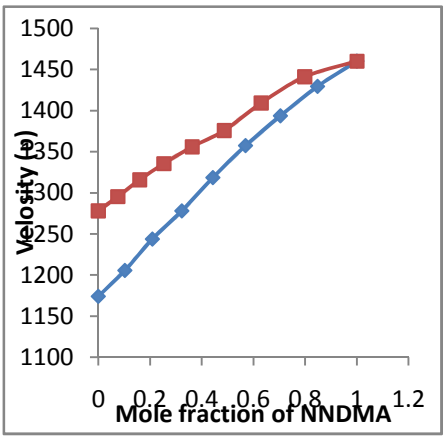

Figure1 (A)

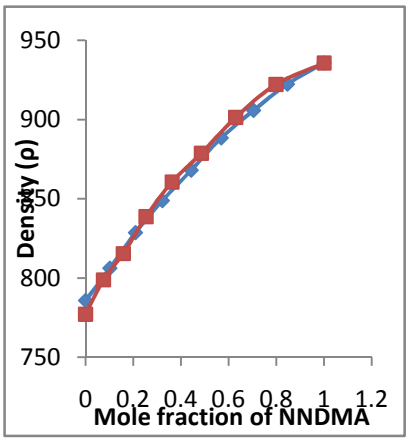

Figure1 (B)

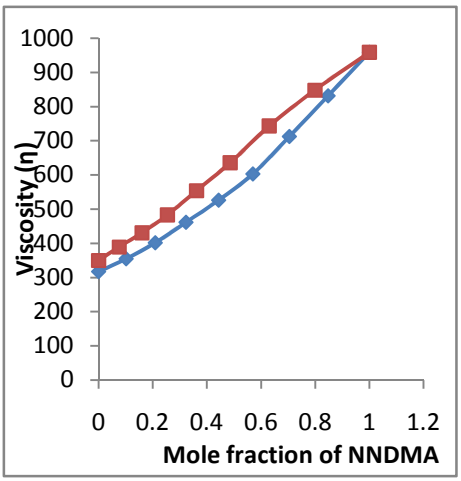

Figure1 (C)

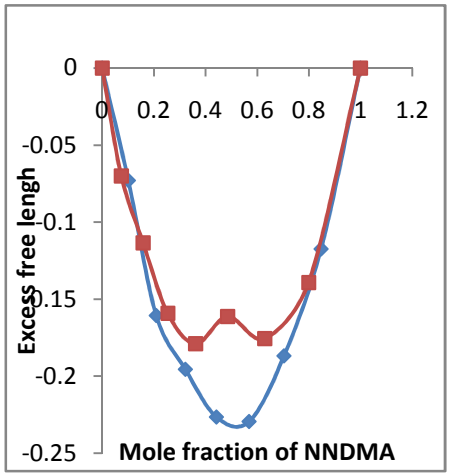

Figure1 (D)
(GFDGZZZZZZZZZZ)

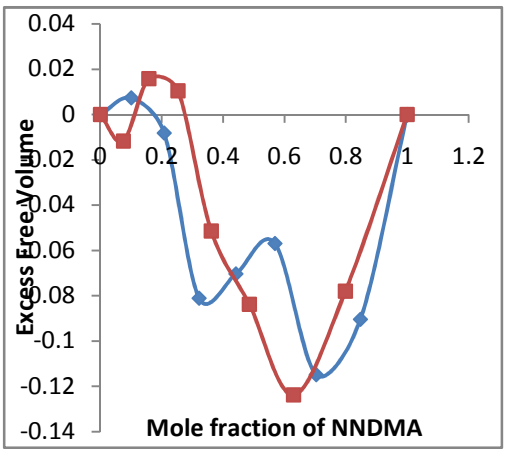

Figure1 (E)

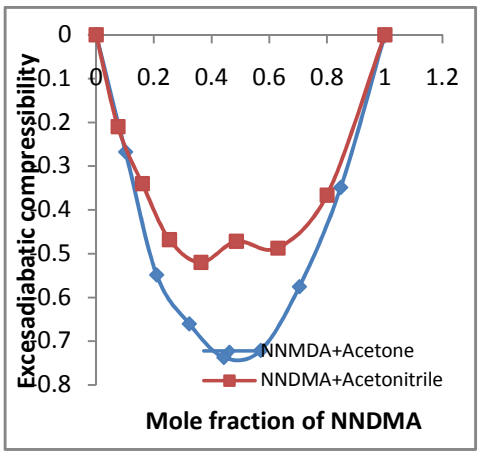

Figure1 (F)

In order to understand the presence of intermolecular interaction between molecules it is essential to study the excess parameters. Table-2 and figures 1(D),1(E)and 1(F) presents the excess free length (L_f^E), excess free volume (V_f^E) and excess adiabatic compressibility (β_α^E)

The values of excess free length (L_f^E)), excess free volume (V_f^E) and excess adiabatic compressibility (β_α^E) are negative in all two systems over the entire range of compositions[12] suggested that the negative excess values have been due to the closely packed molecules which account for existence of strong molecular interaction between unlike molecules.

The negative sign of excess free length (L_f^E), excess free volume (V_f^E) and excess adiabatic compressibility (β_α^E) indicates the strong molecular interaction between the components of NNDMA in acetone and acetonitrile mixtures. According to Fort & Moore,[13] a negative excess value is an indication of strong hetero-molecular interaction in the liquid mixtures in the systems and is attributed to charge- transfer, dipole-dipole, dipole –induced dipole interactions & hydrogen bonding between the unlike compounds, while a positive sign indicates a weak interaction & is attributed to dispersive force which convey that the chances of induced dipole-dipole interactions are overruled & strong dipolar interactions alone are conformed[14-15].

As shown in Table 1 and figure 1, it is observed that the values of excess adiabatic compressibility (β_α^E) and excess free length (L_f^E), are less negative for the NNDMA + acetonitrile system than that of NNDMA + acetone system. This indicates that the less interaction in the former system. Thus it is clear from the above evaluated parameters that there is a strong association between the molecules of the mixture of NNDMA in acetone and acetonitrile.

CONCLUSION

From ultrasonic velocity, density and viscosity measurements, related acoustical parameters and their excess values such as excess adiabatic compressibility β_α^E, excess free length L_f^E and excess free volume V_f^E for the binary liquid mixtures of NNDMA in acetone and acetonitrile mixtures for various concentration at temperature 298.15K, it has been found that the present investigations of thermodynamic parameters are sensitive to the molecular association present in the liquid mixtures. The negative values of excess compressibility (β_α^E), excess free length (L_f^E) and excess free volume V_f^E shows the presence of strong dispersive dipole-dipole interaction between the components of molecule in the mixture. The non-linearity of the curve also supports the interaction exists. The interaction in NNDMA and acetononitrile is weaker than interaction in NNDMA and acetone.

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