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Excess Thermodynamic Properties of Binary Liquid Mixture of N, N-dimethyleacetamide in Benzonitrile through Ultrasonic Measurements at 308.15K and 313.15K

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Abstract: ***The measurements of ultrasonic velocity (υ), density (ρ) and viscosity (η) of the binary liquid mixtures of N, N-Dimethyle acetamide in Benzonitrile have been carried out for the entire range of compositions at temperatures 308.15K and 313.15K. The experimental observed values are used to evaluate thermo dynamical parameters such as adiabatic compressibility (β_α), molecular free length (L_f), acoustic impedance (Z), free volume (V_f), internal pressure (π_i) and their excess values as adiabatic compressibility (β_α^E), free length (L_f^E), free volume (V_f^E), internal pressure (π_i^E), and Gibb's free energy of activation (ΔG^E). From the properties of these excess parameters the nature and strength of the interactions in the binary system have been discussed for molecular interaction. The non linearity nature observed in the plots of these ultrasonic parameters and their excess values with the composition range indicates presence of the intermolecular interaction between the components of the unlike molecules of the mixture. The nature of excess values of the (β_α^E), (L_f^E), (V_f^E), (π_i^E), and (ΔG^E) conforms about the existence of the molecular interaction between the components of the mixture.***

Keywords: Ultrasonic velocity, viscosity, free length, compressibility, internal pressure, molecular interaction, binary mixtures

1. Introduction

The ultrasonic velocity in pure liquid and liquid mixtures is very sensitive to molecular interaction and can be used to understanding the nature and straight of molecular interaction[1,2].This study finds application in several industrial and technological processes. As Ultrasonic investigations of liquid mixtures consisting of polar or non polar components are of importance in many applied fields in understanding the physical nature and strength of molecular interaction in the liquid mixtures[3,4]. Mainly the ultrasonic velocity of liquid is related to the bonding forces between the atoms and molecules and it helps to understand the nature of molecular interactions in pure and binary mixtures of the liquids[5,6]. A literature survey reveals that polar liquids & their mixtures are of great interest to organic chemists to have the knowledge of the type bonds and interactions with each molecule in the liquid mixture such as N,N-dimethyle acetamide and Benzonitrile[7-9]. The excess values of different parameters are very important in order to understand the nature of molecular interactions between the components of the liquid mixtures.

In the present study the ultrasonic velocity, density, and viscosity measurements have been carried out for pure N,N-Dimethyleacetamide and Benzonitrile and their binary mixtures for various concentrations at 308.15K and 313.15 K. The variations of different ultrasonic parameters and their excess values are studied to understand molecular interaction between unlike molecules of the mixtures.

2. Material and Methods

The mixtures of different concentrations of the N, N-Dimethyle acetamide (NNDMA) with Benzonitrile were prepared for different mole fractions. The chemical NNDMA obtained commercially from qualingen having Excel grade 99% purity and Benzonitrile obtained from Merck of AR grade with purity of 99.5% and used without further purification. The measurements of ultrasonic velocities (υ) for different concentrations of pure liquids and binary mixtures were taken on ultrasonic Interferometer of 1MHz (model M-81, Mittal enterprises, New Delhi, India) and it was standardized by using the doubly distilled water. The temperature of the system was maintained constant by using the constant temperature water bath. The measurements of density were carried out by using specific gravity bottle. The Viscosities of the liquid and liquid mixtures are determined by measuring the time of flow of the water and the liquid mixtures at different temperatures by using suspended type viscometer.

The experimentally measured density (ρ) in kgm^{-3}, ultrasonic velocity (υ) in $ms^{-1}$and viscosity (η) in Nsm^{-2} are used to evaluate various parameters like molecular free length (L_f), compressibility (β_α) and acoustic impedance (Z), free volume (V_f) and internal pressure (π_i) by using following relations.

Acoustic impedance $Z = \upsilon \rho$ ---------- 1

Adiabatic compressibility $\beta_\alpha = 1/\upsilon^2\rho$ ----------2

Intermolecular free length $L_f = K \beta_\alpha^{1/2}$ ---------- 3

The free volume $V_f = \left[\frac{M_{eff}}{k\eta}\upsilon\right]^{3/2}$ ----------4

The internal pressure $\pi_i = bRT\left(\frac{k\eta}{\upsilon}\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right)$ ---------- 5

The excess values are determined by using the relation

$A^E = A_{exp} - A_{id}$ ----------6

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.

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 Jacobson's constant ($K=93.875 + 0.375\ T) \times 10^{-8}$ and T being the absolute temperature, k is temperature independent constant which is equal to 4.28×10^9 for all liquids, b stands for cubic packing which is assumed to be 2 for all liquids

3. Result and Discussion

The excess values of different acoustical and thermo dynamical parameters have been calculated from the measurements of ultrasonic velocities, densities and viscosities for the mixtures of NNDMA and benzonitrile for varying mole fractions at 308.15K and 313.15K temperatures. The Tables (1) presented here gives the excess values of different parameters and their corresponding plots are shown in Figure (1). The excess values evaluated have been discussed in light of molecular interactions between the components of binary liquid mixtures as under.

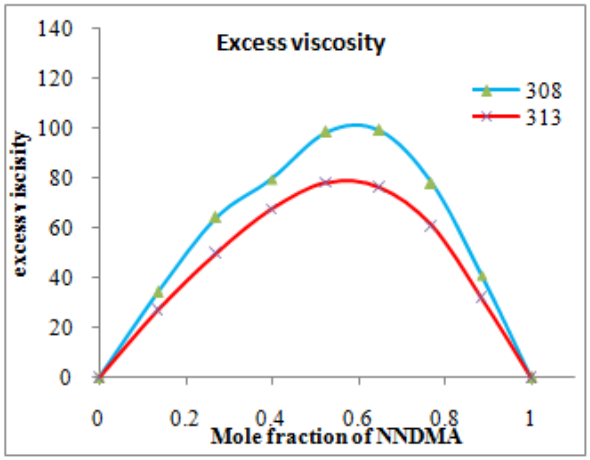
The figure (1) for the excess viscosity (η^E) obtained from the data table (1) is positive in nature; the positive values of excess parameters are the indications of weak interactions between the components of the mixture. The increase in the temperature decreases the excess value of viscosity as should be appeared for the liquids.

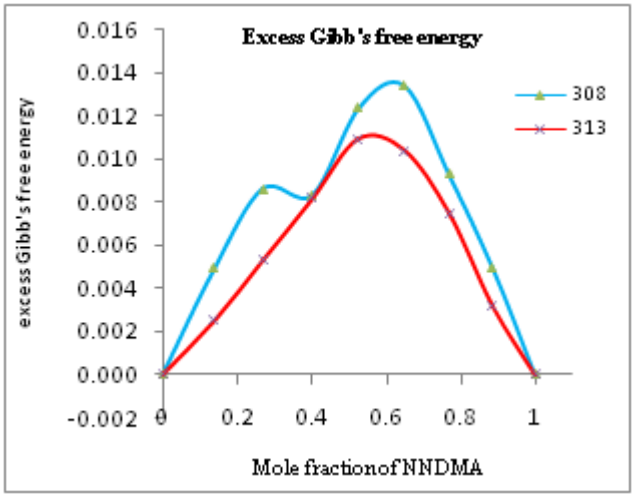
The excess compressibility is reported to be a quantity which is proportional to the strength of interaction between unlike molecules[10]. According to Fort and Moore[11], a negative excess compressibility is an indication of strong molecular interaction in the liquid mixtures while a positive value indicates a weak interaction attributable to dispersion forces. Also, the magnitude of the excess function depends on the relative strength of interaction. The types of interactions between components of different mixtures are charge transfer, hydrogen bonding dipole induced dipole and dipole-dipole interactions.

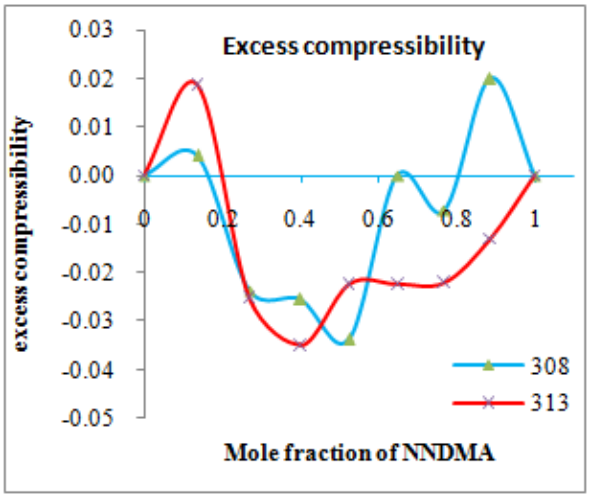
The excess adiabatic compressibility (β_α^E) is mostly negative excepting some small variations for the concentration of NNDMA in the binary mixture. This non linear nature of the excess compressibility is the indication of molecular interaction. The excess compressibility (β_α^E) is negative at 0.2 to 0.6 mole concentration of NNDMA at 308.15K and 0.2 to 1 at 313.15K temperatures, suggesting the strong dipolar interaction occurs between the constituent molecules. The excess free length (L_f^E) is similar to the nature of excess compressibility (β_α^E) at all concentrations and temperatures[12,13] .

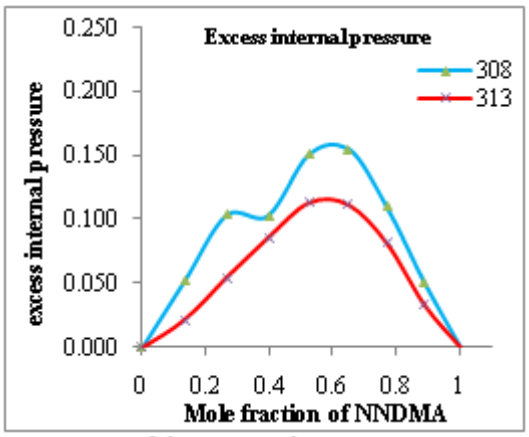
Table 1: Excess values of ultrasonic Velocity (υ^E), viscosity (η^E), adiabatic compressibility (β_α^E), free length (L_f^E), free volume (V_f^E), internal pressure (π_ι^E), and Gibbs free energy(ΔG^E) for NNDMA + Benzonitrile mixture at 308 and 313 K.

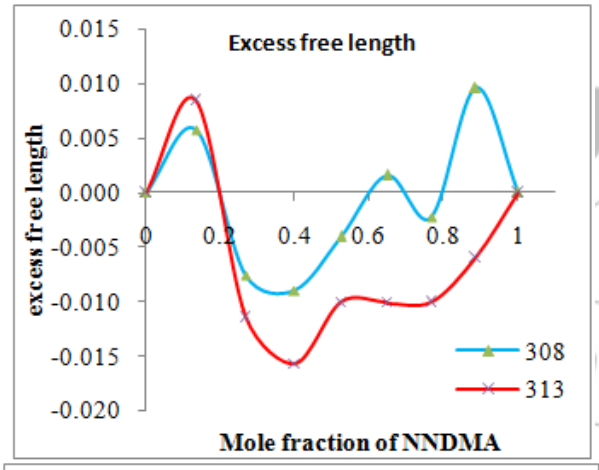
Temp K	Mole fraction NNDMA	Excess viscosity η^E μ Pas	Excess adiabatic compressi $\beta_\alpha^E \times 10^{-10}$ m^2N^{-1}	Excess free length $L_f^E \times 10^{-11}$ m	Ecxess free volume $V_f^E \times 10^{-7}$ m^3/mole	Excess Internal Pressure $\pi_\iota^E \times 10^6$ Pa	Gibbs free energy $\Delta G^E \times 10^{-21}$ KJ $mole^{-1}$
308K	0	0.00000	0.00000	0.00000	0.0000	0.00000	0.00000
	0.13655	34.0548	0.00412	0.00575	-0.0685	0.05256	0.00494
	0.26954	63.9628	-0.02379	-0.00757	-0.1296	0.10370	0.00860
	0.39912	79.3866	-0.02557	-0.00897	-0.1312	0.10315	0.00833
	0.52539	98.5489	-0.03372	-0.00404	-0.1959	0.15113	0.01238
	0.64851	99.0580	-0.00003	0.00161	-0.2016	0.15485	0.01336
	0.76857	77.8811	-0.00723	-0.00224	-0.1483	0.11010	0.00927
	0.88570	41.0177	0.01998	0.00963	-0.0745	0.05096	0.00492
	1	0.00000	0.00000	0.00000	0.0000	0.00000	0.00000
313K	0	0.00000	0.00000	0.00000	0.0000	0.00000	0.00000
	0.13659	27.0539	0.01865	0.00852	-0.0425	0.02198	0.00251
	0.26961	49.9301	-0.02512	-0.01138	-0.1071	0.05429	0.00530
	0.39920	67.2285	-0.03491	-0.01572	-0.1658	0.08633	0.00818
	0.52548	78.1504	-0.02235	-0.01010	-0.2158	0.11334	0.01093
	0.64859	76.4151	-0.02225	-0.01012	-0.2123	0.11192	0.01038
	0.76864	60.7792	-0.02201	-0.00999	-0.1609	0.08175	0.00747
	0.88574	32.1602	-0.01306	-0.00591	-0.0721	0.03300	0.00318
	1	0.00000	0.00000	0.00000	0.0000	0.00000	0.00000











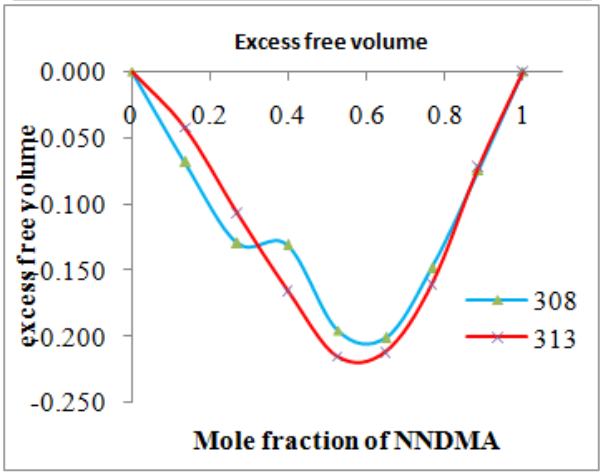


Figure 1: Graphs of Excess values of viscosity (η^E), adiabatic compressibility (β_α^E), free length (L_f^E), free volume (V_f^E), internal pressure (π_ι^E) and Gibbs free energy (ΔG^E) of NNDMA + Benzonitrile mixture at 308.15 and 313.15K.

The opposing tendencies (in various excess parameters) may be due to the fact that strong dipolar interactions and highly directional interaction bonding act simultaneously between the constituent molecules and the relationship between the excess functions is not simple and reflects the properties of the interaction molecules[14]. Free volume being increasing with concentration of NNDMA in the mixture, there is a negative nature of the excess free volume (V_f^E) for all the temperatures. There is no much effect of temperature on the values of excess free volume. The internal pressure is the property of the liquid depends on the density and viscosity as there is increase in the viscosity the internal pressure should show increase because of the closeness of the molecules. The excess internal pressure (π_i^E) here as seen from figure 1 is positive and it decreases with increase in temperatures[15].

The excess Gibb's free energy of activation (ΔG^E) for the system is also showing positive tendency and the nature is depending on the temperature. For higher temperature the excess values are smaller. Positive value of (ΔG^E) can be seen in the binary mixture where specific interactions (hydrogen bonding) between the molecules are dominant where as negative (ΔG^E) indicates behaviour of mixture in which dispersion forces are dominant. According to the excess internal pressure the interactions should be strong but the other parameters which are positive are suggesting the

weak interaction and the forces are dispersive between the components of the mixture. From the positive values of ΔG^E and η^E mostly endothermic type of reaction is suggested in the mixture [12, 13].

4. Conclusion

The density (ρ), ultrasonic velocity (υ), and viscosity (η) have been measured for N, N-dimethyle acetamide and benzonitrile mixtures at 308.15 and 313.15 K to evaluate different thermodynamic parameters. The variations of these parameters indicate the presence of specific interactions between unlike molecules.

In the present study the excess adiabatic compressibility ($\beta_\alpha{}^E$) is mostly negative excepting some small variations for the concentration of NNDMA in the binary mixture. The excess free length ($L_f{}^E$) is similar to the nature of excess compressibility at all concentrations. This non linear nature of the excess compressibility and free length is the indication of molecular interaction. The excess viscosity (η^E) obtained here is positive, the positive values of excess parameters are the indications of weak interactions between the components. There is a negative nature of the excess free volume ($V_f{}^E$). The excess internal pressure ($\pi_i{}^E$) here as seen from figure is positive. According to the excess internal pressure the interactions should be strong but the other parameters which are positive are suggesting the weak dipole-dipole molecular interactions and the dispersive type of forces are exists between the components of the mixture. From the positive values of ΔG^E and η^E mostly endothermic type of reaction is suggested in the mixture.

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References

[1] Eyring H, and Kincaid J F, *J. Chem. Phys*, (1938), 6, 220-229.
[2] Pitzer K S, *Thermodynamics*, 3rd edition (McGraw-Hill book Co, NY (1995)
[3] Kannapan A N, Thirumam S and Palani R, *J. Phys. Science*, (2009), Vol. 20 (2), 97-108
[4] Tabhane V A, Ghosh S and Agrawal S, *J. Pure and Appl. Ultrasonic*, (1900), Vol. 21, 122
[5] Srinivasulu V and Naidu P R, *J. Pure and Appl. Ultrasonic*, (1995), Vol.17, 14-28
[6] Swain K, Priyadarshani P, *Indian J.Pure and Appl. Phys*. (2010) vol.48, Aug 2010, 539 542.
[7] Gupta P K & Stump F B, *Indian J. pure and Appl. Phys.*, (2010), 48, 326- 333.
[8] Arul G & Palaniappan L, *Indian J. pure and Appl. Phys.*, (2005), 43, 755- 758.
[9] Dabrase P B, Suryavanshi B M, Dhawankar S, Patil R A, *All India conference on Global Innovation in Physics*, April 12th - 13th, 2013 C. S. Institute of Technology, Durg, India– 491001, 2013,31-35.
[10] Osamu Kiyohara, Jean-Pierre E Grolier and George C Benson, *Can. J. Chern.* 52, (1974), 2287.
[11] Fort R J and Moore W R, *Trans. Faraday Soc.*, 61 (1965) 2102.
[12] Madhuri N Jaya, Naidu P S, Glory J and Prasad K R, *E-J of Chemistry*, 8(1), 2011, 457-469.
[13] Nithya R, Mullainathan S, Nithiyanantham S and Rajasekaran M, *E-J Chem*. 2009, 6(1), 138-140
[14] Ramanujappa T, Bhavani J A, Rajagopal E and Manohara Murthy N, *Indian J Pure Appl. Phys.* 2000, 38, 301.
[15] Patil R A, Dabrase P B & Suryavanshi B M, *International Journal of basic and applied research*, Jan 2014, 33-38