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Acoustical studies on molecular interactions in binary liquid mixtures at 303K

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ABSTRACT

The acoustical parameters for three binary liquid mixtures namely Acrylonitrile + methanol, Acrylonitrile + cyclohexane and Acrylonitrile +1, 4–dioxane have been measured. From the measured data, some of the acoustical parameters such as adiabatic compressibility (β_a) , free length (L_f), free volume (V_f), internal pressure (π_i), relaxation time (τ) , acoustic impedance(Za) and Gibb's free energy(ΔG)values are computed for the three systems at 303K, from the measures values of ultrasonic velocity(U),density(ρ) and viscosity(η). The behavior of these parameters with composition of the mixture has been discussed in terms of molecular interaction between the components of liquids.

Keywords: Adiabatic compressibility, free length, frees volume, internal pressure, molecular interactions and binary systems.

INTRODUCTION

The ultrasonic study of inter molecular interactions plays an important role in the development of molecular sciences In recent years ultrasonic technique has become powerful tool in providing information regarding the behavior of liquids and solids owing to its ability of characterizing physiochemical behavior of the medium[1]. The study of miscibility and molecular interaction present in polymer and solvent in a polymer solution is of great significance for engineering applications of polymers. They also provide substantial information on the process involving polymer production and their uses [2]. Further, polymer dissolution also plays a key role in many industrial applications in a variety of areas and an understanding of the dissolution process allows for the optimization of design and processing conditions as well as selection of suitable solvent [3]. Many researchers have undertaken these studies qualitatively through ultrasonic velocity, adiabatic compressibility and viscosity measurements [4-12]. However, there are very few studies on the quantitative study of the interactions in a polymer solution system [13**]**. The exhaustive literature survey shows scanty work on pure liquids and liquid mixtures [14, 15]. Acrylonitrile is a versatile fluid and has been used on a wide range of fields and applications**.**

In view of extensive applications of Acrylonitrile ,methanol, cyclohexane & 1,4-dioxane in the engineering process, pharmaceutical industries, present study provides qualitative information regarding the nature and strength of molecular interactions in the liquid mixtures of Acrylonitrile + methanol, Acrylonitrile + p-dioxane and Acrylonitrile + cyclohexane at the temperature 303K through the derived parameters from ultrasonic velocity, density & viscosity measurement. The present investigation is undertaken, in order to study the dependence of the relative strength of intermolecular interaction and their nature in pure liquids and liquid mixtures. The results are discussed in terms of molecular interactions.

2. Theory:

i. Adiabatic compressibility (β_a**)**:
The adiabatic compressibility (βa) has been calculated from the ultrasonic velocity (U) and the density (ρ) of the medium using the equation as:

$$\beta a = 1/ (U^2 * \rho) \quad \text{-------------------- (1)}$$

ii. Intermolecular free length (L_f):
Intermolecular free length has been determined as:

$$\mathbf{L_f = K_J (\beta_a)^{1/2}} \qquad \text{-------------------- (2)}$$

Where K_J is the temperature dependent Jacobson's constant [16, 17**]** but independent of the nature of liquid.

iii. Free volume (V_f):
The free volume [17] has been calculated in terms of ultrasonic velocity (U) and viscosity (η) of the liquid as:

$$\mathbf{V_f = [(Me_{ff}\, U) / (K\, \eta)]^{3/2}} \qquad \text{--------------------- (3)}$$

Where, Meff (Effective mass) = Σ mi xi, in which mi and xi are the molecular weight and the mole fraction of the individual constituents respectively. K is the temperature independent constant, which is equal to $4.28 * 10^9$ for all liquids and η be the viscosity.

iv. Internal pressure (πi):
On the basis of statistical thermodynamics, Suryanarayana [18], derived an expression for the determination of internal pressure (π_i) by the use of free volume concept as:

$$\mathbf{\pi i = (b\, RT)[(K * \eta) /(U)]^{1/2} * [(\rho^{2/3}) / (Me_{ff}{}^{7/6})]} \qquad \text{-----------------(4)}$$

Where, b is the cubic packing which is assumed to be 2 for all liquids and solutions, K is the temperature independent constant , T is the absolute temperature, R is universal gas constant, η be the viscosity and Meff the effective molecular weight .

v. Relaxation time (τ):
Relaxation time **(τ)** is the time taken for the excitation energy to appear as translational energy and it depends on temperature and on impurities. The dispersion of ultrasonic velocity in binary mixture reveals information about the characteristic time of the relaxation process that causes dispersion. The relaxation time (**τ**) can be calculated from the relation as;

$$\mathbf{\tau = (4/3)\, \beta a * \eta.} \qquad \text{--------------- (5)}$$

Where βa and η are adiabatic compressibility and viscosity of the liquid and liquid mixtures.

vi. Acoustic impedance (Za):
The specific acoustic impedance is given by,

$$\mathbf{Za = U * \rho.} \qquad \text{---------------- (6)}$$

Where U and ρ are the ultrasonic velocity and density of the liquid respectively.

vii. Gibb's free energy (ΔG):
The relaxation time for a given transition is related to the activation energy. The variation of relaxation time **(τ)** with temperature (T) can be expressed in the form of Eyring self process theory.

$$\mathbf{1/ \tau = [(K_BT) / h] * \exp (-\Delta G/K_BT).} \qquad \text{--------------- (7)}$$

The above equation can be rearranged as,

$$\mathbf{\Delta G = (- K_BT) \log [h/ (K_BT\tau)].} \qquad \text{---------------- (8)}$$

or, $$\mathbf{\Delta G = (K_BT) \log [(K_BT\tau)/h].} \qquad \text{---------------- (9)}$$

Where K_B is the Boltzmann's constant ($1.3806 \times 10^{-23} Jk^{-1}$), h is the plank's constant (6.63×10^{-34} JS), T is the absolute temperature and **τ** is the relaxation time.

3. Experimental Details:

The component fluid namely Acrylonitrile (AN) (solute) and the methanol, p– dioxane and cyclohexane (solvents) were obtained of Anal R grade, again they were purified and redistilled in accordance with the usual procedure [19] before use. The binary mixture of various mole fractions of two component in the systems, namely Acrylonitrile + methanol, Acrylonitrile +cyclohexane and Acrylonitrile + p – dioxane (hereafter p–dioxane referred as dioxane only), were prepared immediately before use.

The ultrasonic velocity (U) of frequency 10MHz and density (ρ) in these binary mixtures were measured by employing ultrasonic time inter- velometer(UTI -101, Innovative instrument, Hyderabad) and hydrostatic sinker method in the temperature range 10 - 40^{0}C, with an overall accuracy of ±0.1m/s , Ultra thermo state U–10 maintained temperature of the sample constant to ± 0.1˚C. A specially designed and fabricated double walled metallic ultrasonic cell and glass cell along with 6 – digit monopan balance permitted to achieve accuracy of 1 in 10^4 m/s in velocity and 1 in 10^4 gm in density measurement. The viscosity (η) was measured using Ostwald's viscometer with an accuracy of ± 0.0001Nm^{-2}S. All the precautions were taken to minimize the possible experimental error. The setup is checked for standard liquids. The values obtained are compared with Literature [20, 21] values and found that, they match very well with each other.

Table – 1: Comparison of experimental values of density (ρ), viscosity (η) and ultrasonic Velocity (U) of pure liquids at 303K with literature values:

	Pure liquids	**Density (ρ) (Kg m^{-3})**		**Viscosity (η) (10^{-3} NSm^{-2})**		**Velocity (U) (m/s)**	
		Expt.	**Literature**	**Expt.**	**Literature**	**Expt.**	**Literature**
1.	Acrylonitrile	0.8066	---------	0.3060	-------	1425.0	----------
2.	Methanol	776.1	777.7	0.5150	0.5020	1086.0	1087.0
3.	P-Dioxane	1027.4	1028.1	0.8154	1.0100	1324.0	1323.0
4.	Cyclohexane	772.3	763.7	0.6887	0.6895	1240.0	1243.3

Table – 2: The experimental values of density (ρ), viscosity (η) and Ultrasonic Velocity (U) at 303K for the systems - I, II & III:

Mole		**Density (ρ) (Kg m^{-3})**	**Viscosity (η) (10^{-3} Nsm^{-2})**	**Velocity (U) (ms^{-1})**
X1	X2			
System- 1 : Acrylonitrile + Methanol				
0.1	0.9	778.15	0.4918	1119.90
0.2	0.8	783.20	0.4787	1153.80
0.3	0.7	786.35	0.4556	1187.70
0.4	0.6	789.15	0.4324	1221.50
0.5	0.5	793.10	0.4192	1253.50
0.6	0.4	797.15	0.3962	1289.40
0.7	0.3	801.25	0.3730	1323.30
0.8	0.2	803.20	0.3598	1357.10
0.9	0.1	806.00	0.3287	1391.10
System- 2 : Acrylonitrile + P-Dioxane				
0.1	0.9	1004.24	0.8039	1333.00
0.2	0.8	982.22	0.7540	1347.00
0.3	0.7	960.20	0.7045	1359.00
0.4	0.6	938.18	0.6549	1365.00
0.5	0.5	916.12	0.6049	1376.00
0.6	0.4	894.14	0.5549	1387.00
0.7	0.3	872.15	0.5059	1397.00
0.8	0.2	850.12	0.4459	1408.00
0.9	0.1	828.12	0.3855	1416.00
System- 3 : Acrylonitrile + Cyclohexane				
0.1	0.9	776.00	0.6037	1258.00
0.2	0.8	779.70	0.5612	1278.00
0.3	0.7	783.30	0.5187	1297.00
0.4	0.6	787.00	0.5100	1310.00
0.5	0.5	790.70	0.4762	1334.00
0.6	0.4	794.00	0.4337	1353.00
0.7	0.3	797.70	0.3912	1373.00
0.8	0.2	801.40	0.3487	1391.00
0.9	0.1	804.00	0.3400	1410.10

Table – 3: The values of adiabatic compressibility (βa), free length (L_f). Free Volume (V_f), internal pressure (π_i), Acoustic impedance (Z_a), Relaxation time (τ) and Gibb's Free energy (ΔG) at 303 K for the systems: I, II & III respectively.

Mole Frac.		β_a x 10^{-10} (m^2N^{-1})	L_f x 10^{-10} (m)	V_f x 10^{-7} ($m^3.mole^{-1}$)	Лi x 10^6 (Pa.S)	τ x 10^{-12} (s)	Za x10^6 ($kgm^{-2}S^{-2}$)	ΔGx10^{-20} (KJ $mole^{-1}$)
X1	**X2**	**System -1 : Acrylonitrile + Methanol**						
0	1	10.925	0.6594	0.6272	1062.658	0.7502	0.8428	0.2829
0.1	0.9	10.247	0.6386	0.9397	818.182	0.6719	0.8715	0.2629
0.2	0.8	09.591	0.6178	1.3037	661.555	0.6122	0.9037	0.2459
0.3	0.7	09.015	0.5990	1.8064	542.345	0.5476	0.9339	0.2256
0.4	0.6	08.491	0.5813	2.4498	452.277	0.4892	0.9640	0.2052
0.5	0.5	07.990	0.5640	3.1444	388.897	0.4468	0.9965	0.1886
0.6	0.4	07.545	0.5480	4.1260	333.776	0.3986	1.0278	0.1679
0.7	0.3	07.127	0.5326	6.6631	286.971	0.3069	1.0603	0.1203
0.8	0.2	06.760	0.5187	6.6561	255.169	0.3243	1.0900	0.1303
0.9	0.1	06.419	0.5055	8.8631	220.836	0.2814	1.1198	0.1045
1	0	06.109	0.4931	11.3700	194.088	0.2492	1.1486	0.0825
		System -2 : Acrylonitrile + P-Dioxane						
0	1	5.5524	0.4701	1.9341	448.435	0.6034	1.3606	0.2433
0.1	0.9	5.6041	0.4723	2.0353	430.317	0.6007	1.3387	0.2425
0.2	0.8	5.6112	0.4758	2.3221	402.177	0.5641	1.3231	0.2311
0.3	0.7	5.6390	0.4737	2.6576	375.407	0.5297	1.3049	0.2196
0.4	0.6	5.7207	0.4772	3.0471	350.119	0.4992	1.2806	0.2088
0.5	0.5	5.7652	0.4790	3.5378	325.085	0.4698	1.2606	0.1959
0.6	0.4	5.8136	0.4810	4.1532	300.661	0.4301	1.2402	0.1817
0.7	0.3	5.8751	0.4836	4.9141	277.260	0.3963	1.2184	0.1668
0.8	0.2	5.9335	0.4859	5.9211	254.047	0.3607	1.1969	0.1497
0.9	0.1	6.0225	0.4886	7.8220	225.673	0.3067	1.1726	0.1219
1	0	6.1099	0.4931	1.1370	194.409	0.2493	1.1485	0.0825
		System -2 : Acrylonitrile + Cyclohexane						
0	1	8.4211	0.5789	2.1066	371.512	0.7733	0.9576	0.2884
0.1	0.9	8.1429	0.5692	2.4361	350.652	0.7016	0.9762	0.2707
0.2	0.8	7.8526	0.5591	2.8399	330.150	0.6321	0.9964	0.2517
0.3	0.7	7.5506	0.5482	3.3287	311.379	0.5649	1.0211	0.2313
0.4	0.6	7.4043	0.5429	3.9053	291.676	0.5121	1.0309	0.2135
0.5	0.5	7.1068	0.5319	4.2256	281.702	0.4832	1.0548	0.2029
0.6	0.4	6.8799	0.5233	5.6476	253.532	0.3978	1.0743	0.1676
0.7	0.3	6.6500	0.5145	6.9120	235.094	0.3468	1.0952	0.1426
0.8	0.2	6.4491	0.5066	8.5867	216.954	0.2998	1.1147	0.1161
0.9	0.1	6.2561	0.4989	9.3275	209.217	0.2836	1.1336	0.1060
1	0	6.1099	0.4931	11.3700	194.409	0.2493	1.1480	0.0825

RESULTS AND DISCUSSION

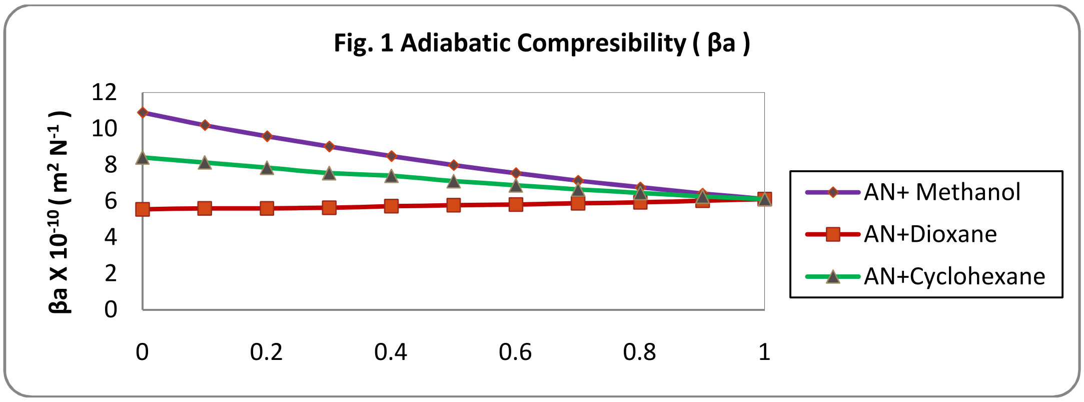
The experimentally measured and literature values [18-20] of density, velocity and viscosity for pure liquids at 303K are presented in Table -1. Experimental density, viscosity and ultrasonic velocity values for the three binary systems namely, system-I: Acrylonitrile + methanol, system-II: Acrylonitrile +dioxane and system–III: Acrylonitrile + cyclohexane respectively at 303K are given in the Table -2. The parameters, adiabatic compressibility(β_a), free length (L_f), free volume(V_f),acoustic impedance (Za), internal pressure (πi), relaxation time (τ) and Gibb's free energy (ΔG) at temperature 303K are listed in Table – 3. The variation of βa**,** L_f and V_f , Vs mole fraction at 303K for the system –I: Acrylonitrile +methanol , system- II : Acrylonitrile + dioxane & system III : Acrylonitrile + cyclohexane are shown in the fig. 1,2 and 3 respectively. The variation of πi, Za & Gibb's free energy (ΔG) Vs mole fraction(x) at 303K for the system - I : Acrylonitrile + methanol, system-II: Acrylonitrile + dioxane and system –III: Acrylonitrile + cyclohexane are shown in the fig. 4, 5 & 6 respectively .

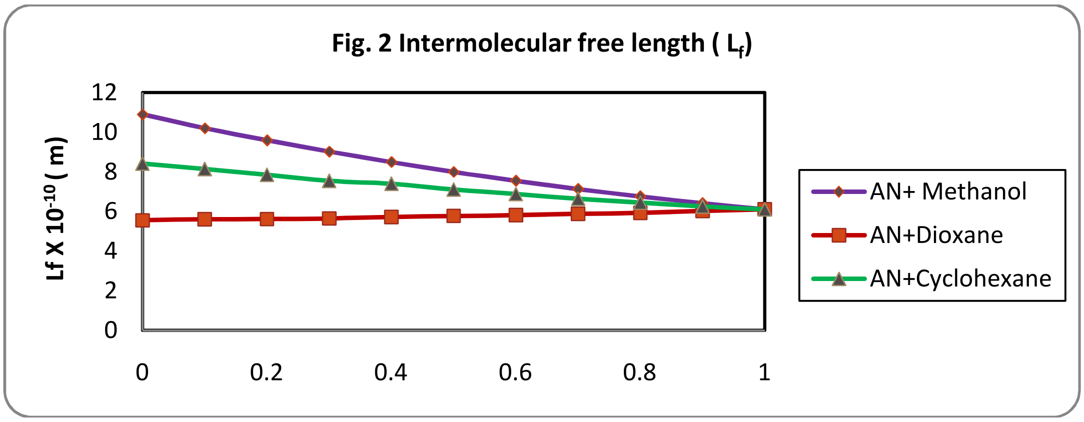
From the Table – 2, it is noted that, the density (ρ) increases with increase in mole fraction for the systems I & III i.e. for Acrylonitrile + methanol and Acrylonitrile + cyclohexane and the density decreases for the system –II i.e. for the system Acrylonitrile + dioxane with increase in mole fraction. Ultrasonic velocity increases and viscosity decreases with increase in mole fraction of the solute in case of the systems – I, II, &III. . The increase in the ultrasonic velocity, in all the systems is due to decrease in adiabatic compressibility and free length in the systems I & III (fig-1 & fig-2). In the system –II (Acrylonitrile +dioxane), velocity increases, but free length decreases in smaller amount (fig 1& fig 2).

It has been observed that for a given concentration, as the number of CH-group or Chain length changes, the sound velocity changes. This may lead to the presence of specific molecular interaction between the molecules of the liquid mixture. The adiabatic compressibility and free length are the deciding factors of the ultrasonic velocity in the liquid systems. The internal pressure decrease (fig.4) and free volume increase (fig.3) with increasing mole fraction of the salute in all the three systems. The internal pressure may gives information regarding the nature and strength of forces existing between the molecules. It represents the presence of weak interaction between the solute and solvent molecules.

Acoustic impedance (Za) increases with increase in the mole fraction of the solute in the systems- I & III and decrease in the system- II (fig. 4). The relaxation time (τ) decreases with increasing the mole concentration of the solute in all the systems. The dispersion of the ultrasonic velocity in the system may contain information about the characteristic time (τ) of the relaxation process that causes dispersion. The relaxation time which is in the order of 10^{-12} sec., is due to structural relaxation process [22] and in such a situation, it is suggested that, the molecules get rearranged due to co-operative process [23].

The Gibb's free energy (ΔG) decreases with increasing mole fraction the solute of all the systems. This may be due to the intermediate compound formation between the binary liquids. It is observed that, generally, the decrease in Gibb's free energy favors the formation of product from reaction. This observation confirms the formation of hydrogen bonding in the binary mixture.





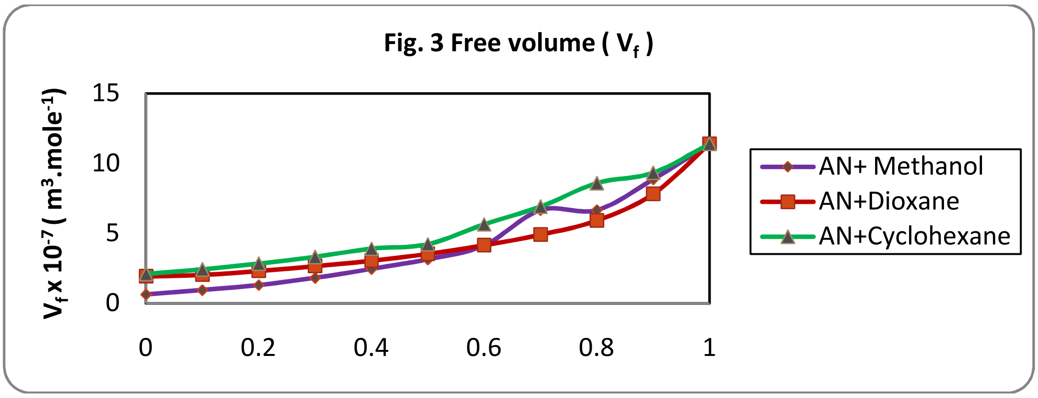


Fig. 4 Internal pressure (∏$_i$)

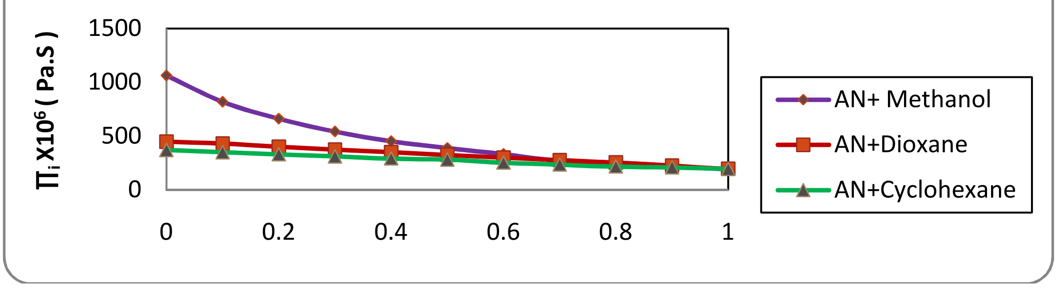


Fig. 5 Rrlaxation time(τ)

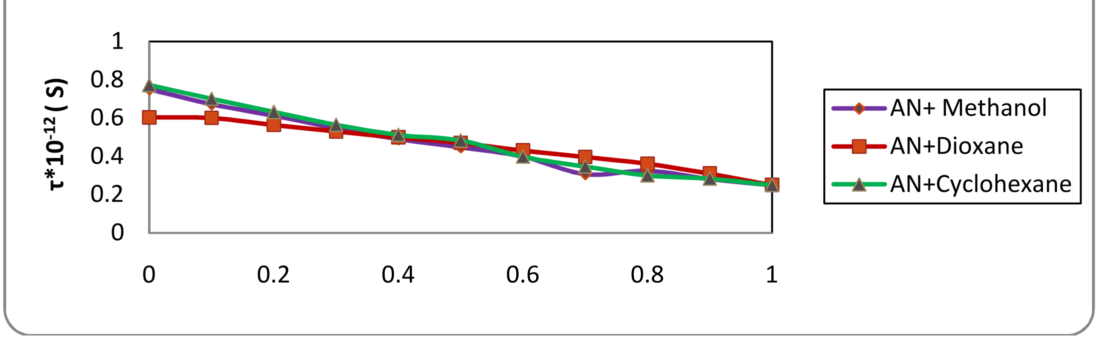


Fig. 6 Acoustic Impedance (Za)

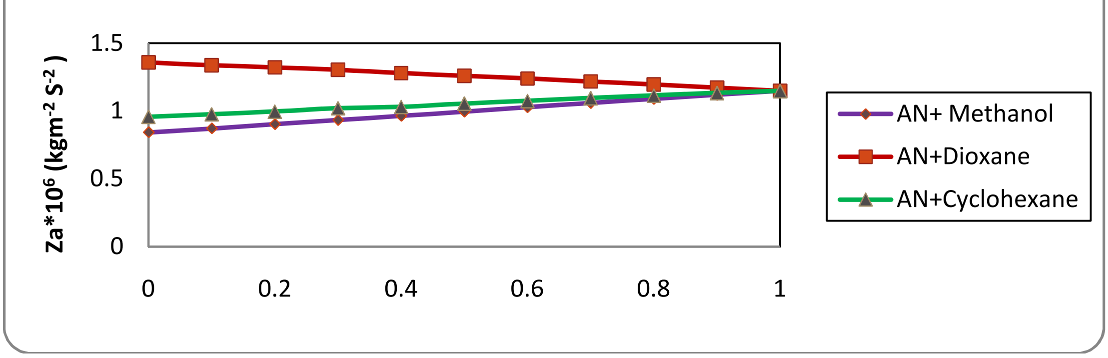
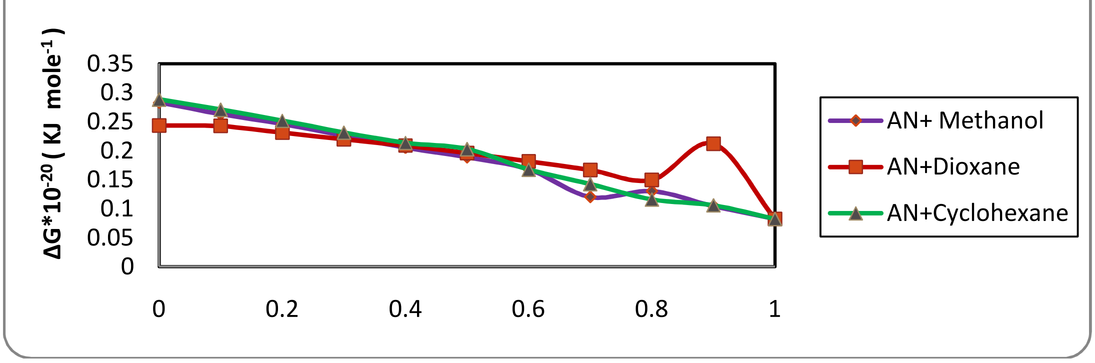


Fig. 7 Gibb's Free Enegy (ΔG)



CONCLUSION

The dependence of ultrasonic velocity and other derived parameters on composition of the mixtures is indication of the presence of molecular interactions. The interaction primarily of dipole-dipole and dipole –induce dipole type and becomes stronger with mole-fraction in Acrylonitrile + methanol system. The molecular interactions present in Acrylonitrile with methanol, dioxane & cyclohexane as a solvent have been studied by viscosity, density and ultrasonic velocity study. Polymer solvent interactions parameters for the systems have been estimated based on Gibb's free energy calculations using data on viscosity and ultrasonic velocity of the solutions, at 303K temperature. The result indicates the existence of molecular interaction between the polymer and the solvent in their solutions. The result is also shows the presence of higher degree of molecular interaction between Acrylonitrile and methanol in solution compared to Acrylonitrile with dioxane and cyclohexane in solutions.

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