



Ultrasonic studies on molecular interactions in the binary mixture of ammonium chloride in polyethylene glycol (600) solution

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ABSTRACT

Densities and ultrasonic velocities have been measured at 303K for the binary mixture of ammonium chloride with polyethylene glycol (600) in different concentrations. From these values, isentropic compressibility (K_s), intermolecular free length (L_p), viscosity (η), internal pressure (π_i), molar volume (V), relaxation time (τ) and classical absorption (α/f^2)_{class} have been calculated and interpreted in terms of intermolecular interactions. Excess parameters and their deviations namely excess isentropic compressibility, excess intermolecular free length and excess viscosity have been calculated. Further theoretical values of ultrasonic velocity in the binary liquid mixture are calculated using three different theoretical models. The relative merits of these theories and relations have been discussed. © 2011 Trade Science Inc. - INDIA

KEYWORDS

Ammonium chloride;
Polyethylene glycol (600);
Molecular interactions;
Excess parameters.

The ultrasonic studies are extensively used to estimate the thermodynamic properties and predict the intermolecular interactions at binary mixtures. The sound velocity is one of those physical properties that help in understanding the nature of liquid state. Using the measured values of sound velocity (U), and density (ρ), the thermodynamic parameters such as isentropic compressibility and intermolecular free length can be computed. Schmelzer et al.^[1] studied the acoustic investigations of pseudo-stable structures in aqueous solutions of polyethylene glycols. They reported structural interactions and the formation of a compact pseudo-stable structure in the region of very low concentration of polyethylene glycol. Syal et al.^[2] studied the ultrasonic velocity, viscosity and density of polyethylene glycols (PEG-

8,000, PEG-20,000) in acetonitrile and water mixtures at 25°C and they concluded that acetonitrile acts as a structure breaker in AN+H₂O solvent system releasing more water dipoles to interact at oxygen sites of PEG chains. Some of the researchers studied the ultrasonic characteristics of aqueous solution of polyethylene glycol^[3-5]. Very few reports are there in the literature on the ultrasonic studies of polyethylene glycol aqueous with salt systems. Kalyanasundaram and Sundaresan^[6] studied the characteristics of PEG + KCl in water system at different temperatures. They observed that the presence of polymer in water decreases the dielectric constant of water and makes the solution a poorer solvent medium for the ions of the salt. An acoustical property of polyethylene glycol with ammonium chloride

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shows that ultrasonic velocity and its derived parameters provide much information on molecular interactions. In the present investigation, ultrasonic velocities, densities and viscosities of polyethylene glycol (of molecular weight 600) with ammonium chloride binary mixture have been carried out. Various derived parameters, such as specific acoustic impedance, isentropic compressibility, intermolecular free length, relaxation time, molar sound velocity, molar compressibility, viscosity and pressure have been evaluated from ultrasonic velocity and density and have been discussed in terms of polymer-solvent interactions.

In the present investigation, ammonium chloride (AR grade—Merck Company) of molecular weight of 53.49 gm/mol was taken and dissolved in water to get 1 N solution. Polyethylene glycol (600) (Merck) is taken and mixed with ammonium chloride solutions of different concentrations. Density, ultrasonic velocity, viscosity were measured in different concentrations of mixed solution at 303K. Ultrasonic interferometer of fixed frequency (2 MHz) was used for measuring ultrasonic velocity. Density of a binary mixture was measured using gravimetric method. These values were found to be accurate up to $\pm 0.1 \text{ kg/m}^3$.

From the observed values of density and velocity, isentropic compressibility, K_s intermolecular free length (L_f), viscosity (η), internal pressure (π_i), molar volume (V), relaxation time (τ), classical absorption (α/f^2)_{class}, deviation in excess isentropic compressibility (K_s^E), excess intermolecular free length (L_f^E) and excess viscosity (η^E) were

calculated from the usual formulas^[7].

The results of measurement of density, velocity, viscosity and excess parameters are given in TABLE 1 and 2. The variation of ultrasonic velocity (Figure 1) in a solution depends upon the increase or decrease of intermolecular free length after mixing the components. On the basis of a model for propagation proposed by Eyring and Kincaid^[8], ultrasonic velocity should decrease if the L_f increases as a result of mixing of components. However, in the mixture of NH_4Cl with polyethylene glycol (600), a decreasing trend in L_f (Figure 2) value and hence the corresponding increasing trend in velocity values are observed with increase in concentration, while at a mole fraction of 0.0995 of PEG(600) a sudden increase in L_f and hence abrupt change in velocity. This non-linear variation indicates the complex formation between constituents of the mixture^[9].

An increase in velocity and acoustical impedance and decrease in isentropic compressibility with increasing concentration suggests the presence of solvent-solute interaction and it is further confirmed by increase in Rao's molar sound function (R) and L_f ^[10,11]. Deviation from the linearity is found in binary mixtures, which demonstrates the presence of molecular interaction between unlike molecules due to adhesive and cohesive forces^[12,27] when the concentration of PEG (600) added to NH_4Cl , it results in considerable decrease in intermolecular space between the molecules as suggested by Jacobsen^[12]. This contributes to decrease in free volume and hence increase in internal pressure.

TABLE 1 : Experimental values of ultrasonic velocity, density, specific acoustic impedance, isentropic compressibility, intermolecular length, effective molecular weight, internal pressure in binary mixture of NH_4Cl in polyethyleneglycol (600)

Mole fraction of NH_4Cl	Mole fraction of PEG(600)	Velocity (U) (m/s)	Density (ρ) (kg/m^3)	Acoustic impedance (Z) ($\text{kg/m}^2\text{s}$)	Isentropic compressibility (K_s) 10^{-10} ($\text{kg}^{-1}\text{ms}^2$)	Free length (L_f) 10^{-10} (m)	Viscosity (η) $\times 10^{-2}$ (Ns/m^2)	Effective molecular weight (M_{eff}) (gms)	Internal Pressure (Π_i) 10^{-4} (pa)
0.9948	0.0052	1600	1041	1665088	3.754	1.227	0.147	59.12	0.743
0.9883	0.0117	1653	1058	1748611	3.459	1.178	0.244	66.09	0.804
0.9801	0.0199	1707	1078	1839728	3.185	1.130	0.490	74.89	0.941
0.9694	0.0306	1760	1108	1950907	2.912	1.081	1.045	86.43	1.115
0.9548	0.0452	1767	1127	1991238	2.843	1.068	1.146	102.15	0.959
0.9337	0.0663	1773	1141	2022802	2.788	1.057	2.573	124.86	1.132
0.9005	0.0995	1733	1136	1968352	2.931	1.084	3.611	160.57	1.034
0.8408	0.1592	1685	1134	1910996	3.105	1.116	4.783	224.87	0.838
0.7013	0.2988	1680	1132	1902096	3.129	1.120	6.413	375.10	0.504

TABLE 2 : Computed values of molar volume, molar compressibility, molar sound velocity, available volume, free volume, relaxation, classical absorption co-efficient of NH_4Cl in polyethylene glycol (600)

Mole fraction of NH_4Cl	Mole fraction of PEG(600)	Molar volume (V) 10^{-3} (m^3/mol)	Molar sound velocity (R) (m^3/mole) (m/s) ^{1/3}	Molar compressibility (W) (m^3/mole) ($\text{Kg}^{-1}\text{ms}^2$)	Available volume (V_a) $\times 10^{-1}$ (m^3/mole)	Free volume (V_f) 10^{-3} (m^3/mole)	Relaxation time (τ) 10^{-11} (s)	Classical absorption (a/f^2) _{class} 10^{-13}
0.9948	0.0052	0.568	0.665	1.246	0.568	1.851	0.073	0.090
0.9883	0.0117	0.625	0.739	1.403	0.645	1.070	0.113	0.134
0.9801	0.0199	0.695	0.830	1.458	0.741	0.476	0.208	0.240
0.9694	0.0306	0.778	0.939	1.792	0.856	0.198	0.406	0.455
0.9548	0.0452	0.906	1.096	2.094	1.000	0.223	0.434	0.485
0.9337	0.0663	1.095	1.325	2.536	1.213	0.090	0.957	1.064
0.9005	0.0995	1.414	1.698	3.253	1.532	0.076	1.411	1.605
0.8408	0.1592	1.983	2.360	4.525	2.089	0.078	1.980	2.317
0.7013	0.2988	3.313	3.938	7.551	3.479	0.110	2.676	3.141

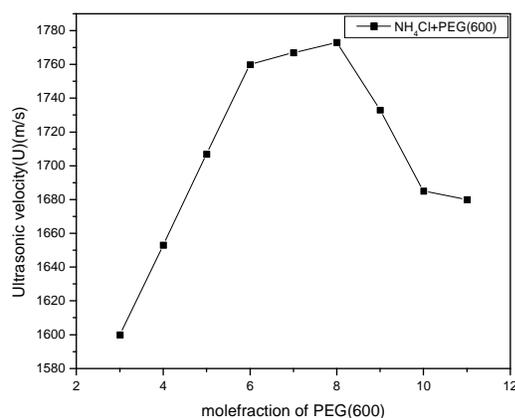


Figure 1 : Variation of Ultrasonic velocity with mole fraction of PEG (600) of binary mixture

When dissolved in water, NH_4Cl_2 form NH_4^{++} and Cl^- ions. These ions are strongly bonded with water molecules. The ionic radii of Cl^- are 1.81 \AA ^[13]. In the case of polyethylene glycols, the basis unit is ethylene glycol which consists of two hydrophilic hydroxyl groups and a hydrophobic hydrocarbon ($-\text{CH}_2\text{CH}_2-$) group. Hence polymerization of ethylene glycol groups takes place by the elimination of H_2O molecules. The ethylene group of molecules forms hydrogen bond with water molecules.

At the beginning, the ultrasonic velocity increases with concentration and corresponding decrease in L_f . There is a strong interaction between NH_4^{++} , Cl^- and $-\text{CH}_2\text{CH}_2-$ group of molecules and hence, L_f decreases and leads to a decrease in this compressibility. This behavior may collapse at higher concentration of PEG

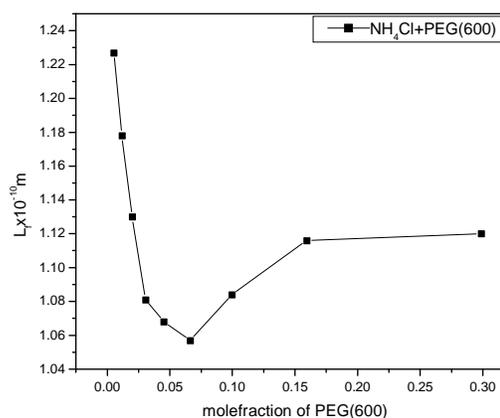


Figure 2 : Variation of intermolecular free length with mole fraction of PEG (600) of binary mixture.

(600) with a mole fraction of 0.9005 of NH_4Cl . It may be due to the extended structure of PEG with Cl^- and NH_4^{++} molecules. And at higher concentration some formations of free water molecules disturbed uniformly throughout the solution and hence decrease in velocity. This decrease in compressibility results in the increase in velocity.

The deviation in isentropic compressibility can be explained^[14,24] by taking in to consideration of the following factors.

1. Loss of dipolar association and difference in size and shape of the component molecules which lead to a decrease in velocity and an increase in compressibility.
2. Dipole-dipole interaction or hydrogen bonded complex formation between unlike molecules which leads

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to an increase in sound velocity and a decrease of compressibility. The actual deviation depends on the resultant effect. In the present study, compressibility decreases (Figure 3) with increase the concentration of PEG (600) indicating hydrogen bond formation which collapses at higher concentration. This result is further supported by viscosity measurements.

The viscosity is found to exhibit linear variation (Figure 4) with concentration of PEG (600). The viscosity of a binary mixture may be due to the formation of intermolecular association by hydrogen bonding between the ethylene glycol molecules and NH_4^+ [15].

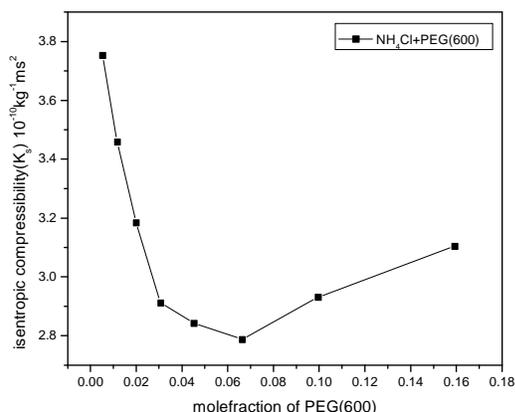


Figure 3 : Variation of isentropic compressibility with mole fraction of PEG (600) of binary mixture

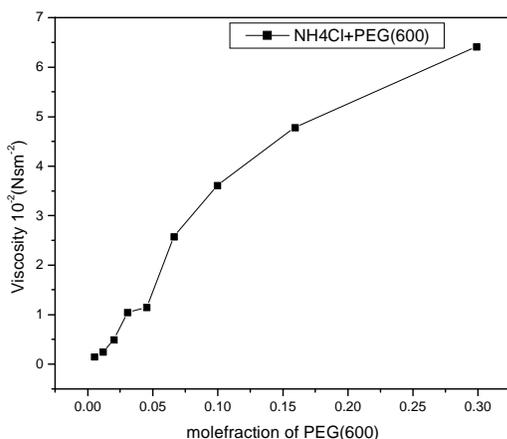


Figure 4 : Variation of viscosity with mole fraction of PEG (600) of binary mixture

The internal pressure is the resultant of the forces of attraction and repulsion between the molecules in a liquid. The repulsive forces become prominent showing relatively lower values of internal pressure. When one of the components is large in ratio the internal pressure values are high, predicting greater forces of attrac-

tion between the molecules. Internal pressure is maximum where the intermolecular association is strongest [16]. Free volume decreases with concentration. It decreases linearly and it is minimum at a mole fraction of 0.0995 of PEG with a mole fraction of 0.9005 of NH_4Cl . The presences of minima in free volume at a composition confirm the presence of complex formation [17].

Hirchfelderetal [18] found that free volume (V_f) of a molecule at a particular concentration and pressure, depends only on the internal pressure of the liquid. The weakening molecular association leads to a large free volume available for molecular motion and the reverse effect give rise to smaller free volume. Thus the effect of concentration on internal pressure and free volume has been studied. As internal pressure is known to be an inverse function of free volume, the trend of the plots of free volume confirms the same [19,20]. Relaxation time, classical absorption also supports the above discussion. These properties show a linear increase with concentration [21].

From the Figure 5, it is observed that the negative excess compressibility in all compositions of a binary mixtures indicate that the hydrogen bond formation dominates in all concentrations. In the study of the binary mixtures of NH_4Cl , and PEG (600), the non-linear variations of excess compressibility shows that H_2 bond interaction are more strong up to the mole fraction of 0.9337 NH_4Cl and above that it decreases and this is confirmed by viscosity study. It is also observed that the L_f^E shows a negative value in all the compositions. There is a linear increase with the concentration and is maximum at the composition at 0.9337 at NH_4Cl above which it decreases. It shows

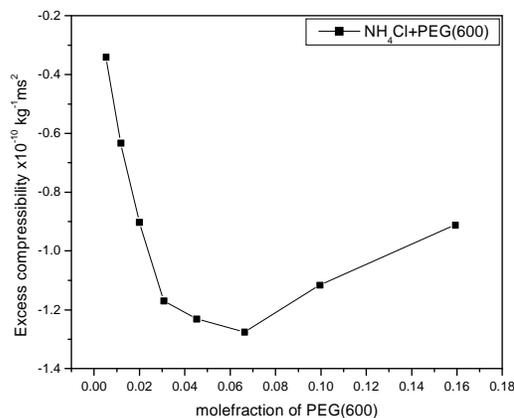


Figure 5 : Variation of excess compressibility with mole fraction of PEG (600) of binary mixture

that strong molecular interaction between the components through their dipoles^[22].

TABLE 3 : Computed values of excess parameters of binary mixture of ammonium chloride in polyethylene glycol (600)

Mole fraction of NH ₄ Cl	Mole fraction of PEG	Excess compressibility (K_s^E) $\times 10^{-10}$ ($\text{kg}^{-1}\text{ms}^{-2}$)	Excess free length (L_r^E) 10^{-10} (\AA)	Excess viscosity (η^E) 10^{-2} (Ns/m^2)
0.9948	0.0058	-0.34047	-0.546	0.13328
0.9883	0.0117	-0.63207	-1.030	0.18779
0.9801	0.0199	-0.90192	-1.204	0.25671
0.9694	0.0306	-1.16948	-1.985	0.34704
0.9548	0.0452	-1.23109	-2.103	0.47006
0.9337	0.0663	-1.27538	-2.196	0.64786
0.9005	0.0995	-1.11557	-1.898	0.92761
0.8408	0.1592	-0.91129	-1.529	1.43065
0.7013	0.2988	-0.81653	-1.375	2.60653

According to Fort and Moore^[23] excess viscosity tends to become more positive as the strength of interaction increases. The excess viscosity variation gives a qualitative estimation of the strength of intermolecular interactions. The excess viscosities^[24] may be generally explained by considering the following factors.

1. The difference in size and shape of the component molecules the loss of dipolar association in pure component may contribute to a decrease in velocity and
2. Specific interaction between unlike components such as hydrogen bond formation and charge transfer complexes may cause for an increase in the viscosity in mixtures than the pure components.

The former effect produces deviation in excess viscosity and the latter produce positive deviation in excess viscosity. The excess viscosity is generally considered as a result of above two major effects. From the Figure 7, it can be observed that the excess viscosity values are positive and it linearly increases with concentration as the strength of interaction between the unlike molecules increases. In the present study, the excess viscosity is positive, due to di-polar forces, indicating a strong interaction between the unlike molecules^[24,25].

Theoretical values of ultrasonic speed in the present binary mixtures were evaluated using different theories. Comparisons of theoretical values of ultrasonic speeds with these obtained experimentally in the present binary liquid mixtures is expected to reveal the nature of inter-

action between the component molecules in the mixtures. Such a theoretical study is useful in building the comprehensive theoretical model for the liquid mixtures.

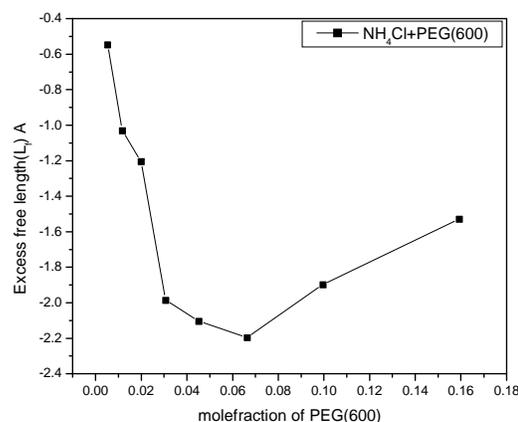


Figure 6 : Variation of excess free length with mole fraction of PEG (600) of binary mixture

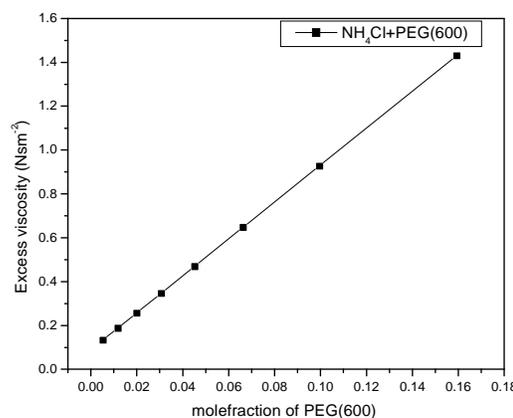


Figure 7 : Variation of excess viscosity with mole fraction of PEG (600) of binary mixture

TABLE 4 : Computed values of theoretical velocity using free length theory (FLT), Nomoto's relation and impedance dependent relation (IDR) and percentage of deviation in the binary mixture of ammonium chloride in polyethylene glycol (600)

Mole fraction of NH ₄ Cl	Mole fraction of PEG	U _{exp} (m/s)	U _{FLT} (m/s)	U _{Nomoto} (m/s)	U _{IDR} (m/s)	Percentage of Deviation		
						FLT	Nomato	IDR
0.9948	0.0052	1600.00	1599.87	1600.33	1600.00	0.00812	0.0206	0
0.9883	0.0117	1653.33	1653.02	1653.69	1653.33	0.0188	-0.0218	0
0.9801	0.0199	1706.66	1706.89	1706.69	1706.66	-0.0135	0.0018	0
0.9694	0.0306	1760.00	1759.55	1759.84	1760.00	0.0256	0.0091	0
0.9548	0.0452	1766.66	1766.20	1766.61	1766.66	0.0260	0.0028	0
0.9337	0.0663	1773.33	1773.91	1773.30	1773.33	-0.0034	0.0017	0
0.9005	0.0995	1733.33	1733.59	1733.26	1733.33	-0.0150	0.0040	0
0.8408	0.1592	1685.33	1685.15	1685.35	1685.33	0.0107	0.0012	0
0.7013	0.2988	1680.00	1680.38	1679.95	1680.00	0.0226	0.0030	0

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Theoretical values of ultrasonic speed in the mixtures at different mole fractions were calculated using the usual relations. A close perusal of TABLE 3 indicates the deviations of theoretical evaluation using FLT, Nomoto and IDR. From the results, it is observed that, more deviations in the FLT and Nomoto method and it is found that IDR method is best suited with experimental results and followed by Nomoto relations^[26,27].

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