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Acoustic and Viscometric Studies on Aqueous N-1-Naphthyl Ethylene Diamine Dihydrochloride

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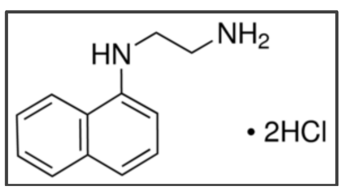
ABSTRACT

The acoustic and viscometric studies are being increasingly used as tools for investigation of the properties of pure components and the nature, strength and order of intermolecular interactions between the constituents in solutions. The density, viscosity and ultrasonic velocity of aqueous N-1-Naphthyl Ethylene Diamine Dihydrochloride of different concentrations at 298.15 K and 300.15 K have been studied. From the experimentally measured data, various thermo acoustic parameters such as adiabatic compressibility, free length, free volume, internal pressure, acoustic impedance, relaxation time, molar sound velocity and Gibb's free energy have been evaluated. In terms of these thermo acoustic parameters, the molecular interactions between the components of this system were also discussed.

Graphical Abstract



N-1-Naphthyl ethylenediamine dihydrochloride

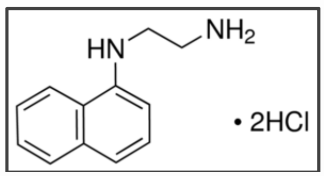
Keywords: Ultrasonic velocity, Molecular interactions, Free length.

INTRODUCTION

In recent years, ultrasonic field have received the status of an important inquest to study the properties of sciences, industries, metallurgy and also in medicine [1-2]. Ultrasonic studies are appropriate tool for studying the physicochemical properties [3-5] of the system. The variation of ultrasonic parameters with concentration and temperature in liquid mixtures and solutions helps us in better understanding in phenomenon of molecular aggregation. Ultrasonic velocity is temperature dependent quantity in most of the solutions. It also depends on the concentration of the solute used. The measurements of density, viscosity and related thermodynamic parameters are used to explain the nature, strength and order of the molecular interactions. The molecular interactions studies can be carried out by spectroscopic methods [6], the other non-spectroscopic methods such as dielectric [7], ultrasonic velocity and viscosity [8] measurements have been widely used. Ultrasonic technique is widely used over these methods because of low cost, easy to use, less time consuming and it gives more precise results. In the present work, an attempt has been made to examine the variety of thermodynamic properties of aqueous N-1-Naphthyl ethylenediamine dihydrochloride to variation in temperature, size, shape and nature of the mixture from the graphical and analytic perspectives in order to understand the nature and other important patterns of molecular interactions that exist in liquid mixture.

MATERIALS AND METHODS

N-1-Naphthyl ethylenediamine dihydrochloride AR 99%, an amino acid (CAS No.1465-25-4) having molecular weight of 259.18 was obtained from LOBA Chemie, India. The appearance of this chemical is almost white powder becoming pink on exposure to light having Assay Min 99%. The compound was having an N-(1-naphthyl) substituent. It is used as a coupling agent for the spectrophotometric determination of amino phenols, phenylenediamines, dinitroanilines, chloroanilines, thiols and sulphonamides. The molecular structure of this compound is as follows



The ultrasonic velocities of the solution under the study were measured by using digital ultrasonic pulse echo velocity meter (VCT -70A). Digital ultrasonic pulse echo velocity meter is a simple and unique, direct reading digital system to determine the velocity of ultrasonic waves as well as to observe echoes for attenuation measurements with excellent accuracy. One piezo – electric transducer is provided at the end of the liquid cell to generate and receive the ultrasonic echo waves through the solutions under observation. The temperature around the cell was controlled by circulating the water from thermostat manufactured by Acculab scales company (Model – i-therm, AI–7982). The water was allowed to circulate through the double walled measuring cell which was useful to obtain the desired temperature. The density of the stock solution was measured by using highly accurate specific gravity bottle method. To determine the viscosity of the solutions, an Ostwald's type viscometer is used. The viscometer was set with fresh water immersed in the water bath which was kept at the experimental temperature. The flow time was measured by using a digital stop watch having high accuracy. The temperature around the viscometer was maintained by using the same temperature controller.

Mathematical Formulation

Acoustic Impedance (Z): The specific acoustic impedance is given by

$$Z = U\,\rho_s (Kgm^{-2}s^{-1})$$

ρ_s = Density of solution
U = ultrasonic velocity of solution

Adiabatic Compressibility (β):

$$\beta_{ad} = \frac{1}{U^2 \rho_s} (N^{-1}m^2)$$

Free Length (L_f):

$$L_f = K_T\, \beta_{ad}^{1/2} \ (m)$$

Where, K_T istemperature dependent constant (93.875+0.375T)10^{-8}

Free Volume (V_f):

$$V_f = \left(\frac{M_{eff}U}{k\eta}\right)^{3/2} (m^3mol^{-1})$$

Where, M_{eff} = Molecular Weight
k is temperature independent constant (4.28×10^9)

Internal Pressure (π_i):

$$\pi_i = bRT\left(\frac{k\eta}{U}\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right) \qquad (Pa)$$

b = 2 for all liquids
R = Gas const (8.314)
T is temperature in Kelvin
k is temperature independent constant (4.28×10^9)

Molar volume (V_m):

$$V_m = \frac{M_{eff}}{\rho} \ (m^3.mol^{-1})$$

Molar sound velocity (R):

$$R = \frac{M_{eff}}{\rho}(U)^{1/3} \ (m^5N^{-1})$$

Relaxation Time (τ):

$$\tau = \frac{4\eta\beta}{3} \ (Sec)$$

Gibb's free energy: The Gibb's free energy can be estimated from the following relation.

$$\Delta G = -kT\log\left[\frac{h}{\tau KT}\right] (Jmol^{-1})$$

RESULTS AND DISCUSSION

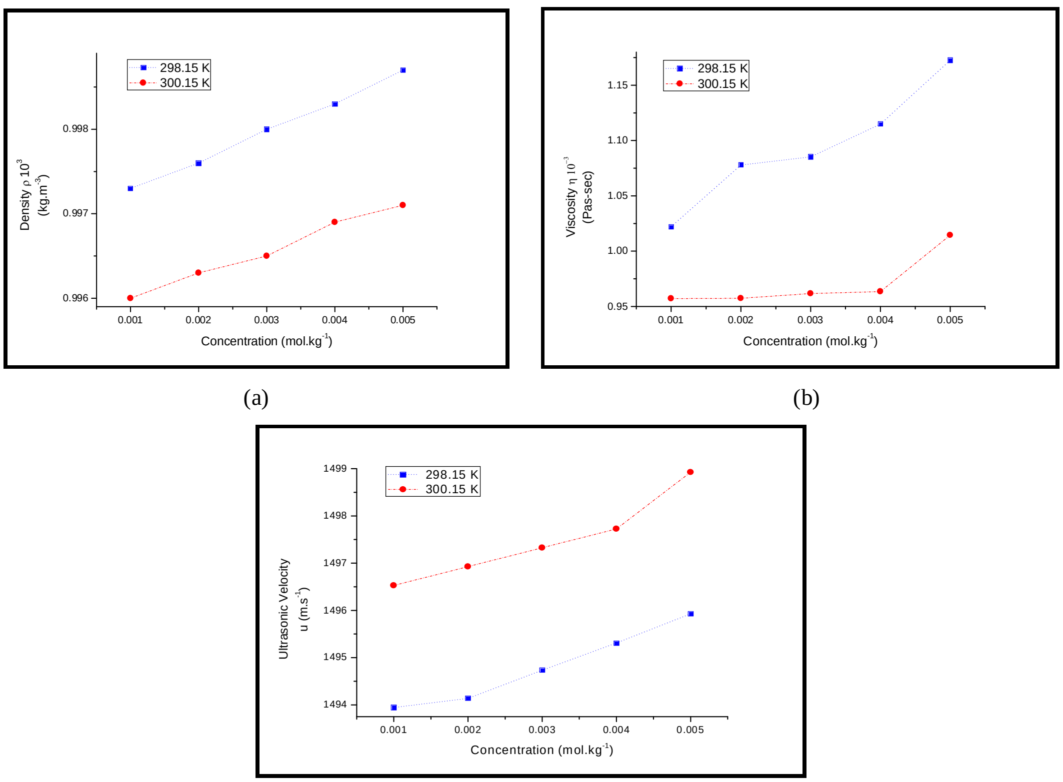
The observed values of densities, viscosities and ultrasonic velocities of aqueous N-1-naphthyl ethylene diamine dihydrochloride for different concentrations from 0.001 to 0.005 mol kg^{-1} at 298.15 K and 300.15 K are presented in table 1. For systematic understanding the effect of concentration and temperature on these parameters, the graphs have been plotted and they are shown in fig. 1(a-c).
Fig.1(a) shows the variation of density of aqueous N-1-Naphthyl ethylene diamine dihydrochloride solution which is increasing with rise in concentration and decreasing with increasing temperature followed the expected result, as solute particles increases in the solution the density increases. We know that volume is directly proportional to temperature, so it follows the trend that at higher temperature the density of aqueous solution decreases. Thus it shows that the density of aqueous solution has no influence on molecular aggregation phenomenon [9].

Table 1. Experimental data of density, viscosity and ultrasonic velocity of aqueous N-1-naphthyl ethylene diamine dihydrochloride at 298.15 K and 300.15 K

Concentration ($mol.kg^{-1}$)	Temperature	0.001	0.002	0.003	0.004	0.005
Density $\rho\ 10^3\ (kg.m^{-3})$	298.15K	0.9973	0.9976	0.9980	0.9983	0.9987
	300.15K	0.9960	0.9963	0.9965	0.9969	0.9971
Viscosity, $\eta\ 10^{-3}$(Pa-s)	298.15K	1.0221	1.0779	1.0853	1.1148	1.1726
	300.15K	0.9571	0.9574	0.9617	0.9634	1.0144
Ultrasonic Velocity, u ($m.s^{-1}$)	298.15K	1493.943	1494.136	1494.733	1495.331	1495.929
	300.15K	1496.528	1496.927	1497.326	1497.726	1498.927

Viscosity (η) defined as the resistance per unit area of a fluid to flow. Fig. 1(b) shows viscosity of solution increasing with respect to concentration and decreasing with increasing temperature. Intermolecular attractive forces do not permit a free flow of molecules in liquid. At lower temperature, viscosity is found greater because of intermolecular forces due to increase in solute which cause attraction between the solvent and solute it shows the structure making capability [10] of solute in the solution. With increasing temperature there is weakening of cohesive forces that result in decrease in viscosity.

The ultrasonic velocity of understudied aqueous solution is increasing with respect to concentration and temperature as shown in Fig. 1(c). The increase in velocity indicates that the weakening of solute-solvent interactions [11] at higher temperature. Because of increase in density and viscosity shows that decrease in compressibility of the solution and mainly the velocity depends on the elastic properties of the solution. It also suggests there is no complex formation [12] is present in solution. Similar trend is reported [13-15] for various aqueous solutions.



(a) (b)

(c)

Figure 1. Effect of concentration and Temperature on (a) Density (b) Viscosity (c) Ultrasonic Velocity of aqueous N-1-naphthyl ethylene diamine dihydrochloride.

The hydrogen bonding between the like or unlike components are in solution increases or decreases due to compressibility. Adiabatic compressibility simplifies the understanding of the physicochemical properties of the solution. Increasing the concentration of the solution makes it denser so the hydrogen bonding decreases [16]. In present investigation it follows the same trend shown in fig. 2(a).

The surface to surface distance between two neighboring molecules is known as free length. If the free length decreases [17] then the solute shows structure breaking properties in the solution and vice versa. In present investigation as ultrasonic velocity increases while the free length decreases with concentration and temperature respectively. The space between two surfaced molecules is decreased

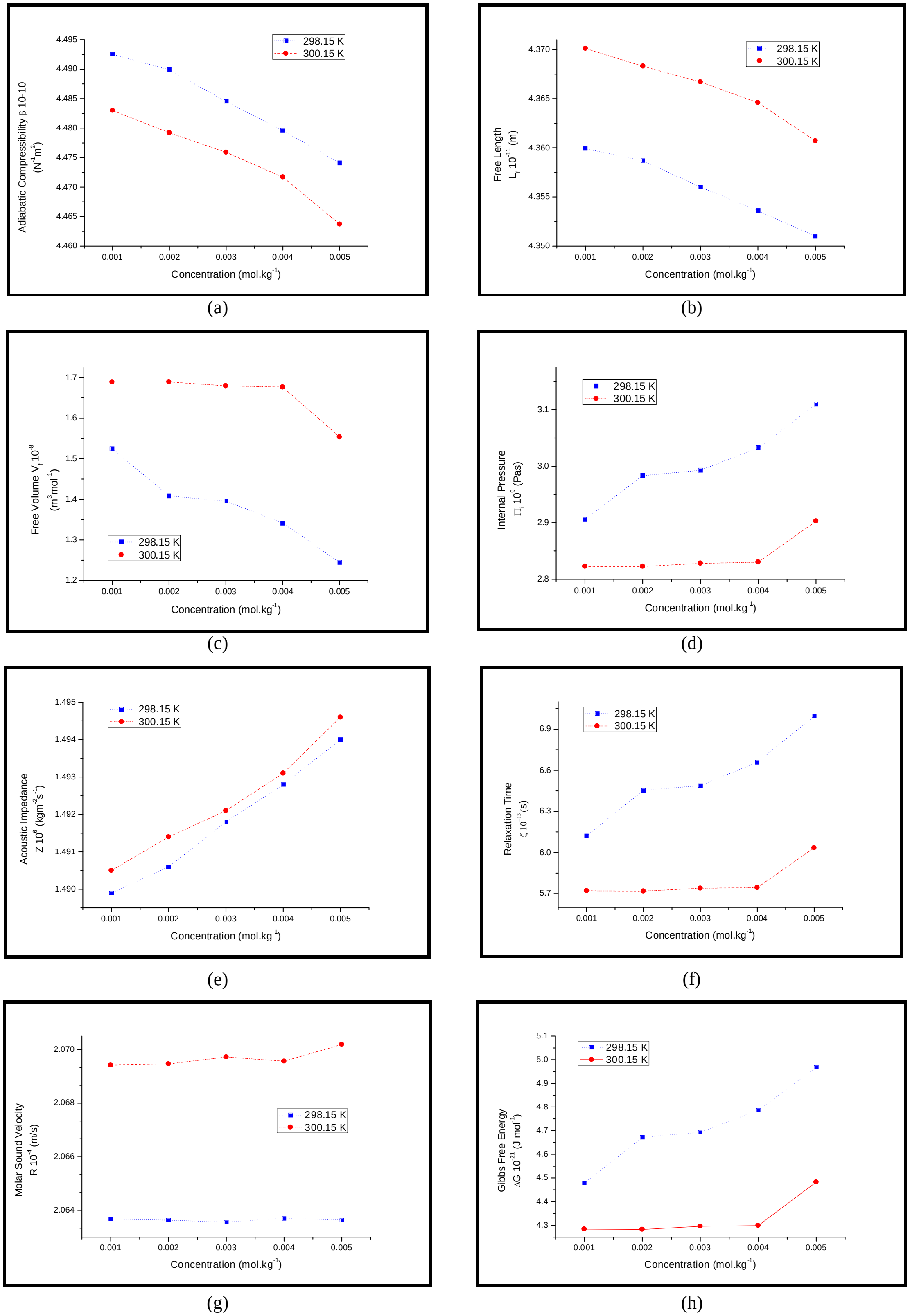


Figure 2. Effect of Adiabatic compressibility, Free length, Free volume, Internal pressure, Acoustic impedance, Relaxation time, Molar sound velocity, Gibbs free energy of aqueous N-1-naphthyl ethylene diamine dihydrochloride

hence the solute understudy shows structure making property. The variation of free length with concentration and temperature are shown in fig. 2(b).

Table 2. Evaluated thermodynamic parameters of aqueous N-1-naphthyl ethylene diamine dihydrochloride at 298.15 K and 300.15 K

Concentration (mol.kg^{-1})	Temperature	0.001	0.002	0.003	0.004	0.005
Adiabatic Compressibility	298.15K	4.4925	4.4899	4.4845	4.4796	4.4741
β 10-^{10} ($N^{-1}m^2$)	300.15K	4.4830	4.4792	4.4759	4.4717	4.4637
Free length	298.15K	4.3599	4.3587	4.3560	4.3536	4.3510
L_f 10^{-11}(m)	300.15K	4.3701	4.3683	4.3667	4.3646	4.3607
Free Volume	298.15K	1.5247	1.4086	1.3956	1.3418	1.2450
V_f 10^{-8} (m^3mol^{-1})	300.15K	1.6892	1.6895	1.6796	1.6764	1.5539
Internal Pressure	298.15K	2.9055	2.9833	2.9929	3.0325	3.1095
π_i 10^9(Pas)	300.15K	2.8226	2.8226	2.8281	2.8302	2.9026
Acoustic Impedance	298.15K	1.4899	1.4906	1.4918	1.4928	1.4940
Z 10^6 ($kgm^{-2}s^{-1}$)	300.15K	1.4905	1.4914	1.4921	1.4931	1.4946
Relaxation Time	298.15K	6.1221	6.4527	6.4892	6.6584	6.9952
Ϛ 10^{-13}(s)	300.15K	5.7207	5.7181	5.7392	5.7441	6.0347
Molar Sound Velocity	298.15K	2.06368	2.06363	2.06356	2.06370	2.06364
R 10^{-4}($m\ s^{-1}$)	300.15K	2.06941	2.06946	2.06972	2.06956	2.07019
Gibbs Free Energy	298.15K	4.4795	4.6723	4.6931	4.7874	4.9684
ΔG 10^{-21} (J mol^{-1})	300.15K	4.2837	4.2821	4.2957	4.2988	4.4827

The strong association between solute and solvent molecules by means of strong hydrogen bonding similar to the results of Giratkar *et. al* [**18**]. The decrease in free volume with concentration may be due to decreasing space between solute and solvent molecules by means of stronger hydrogen bonding. Fig. 2(c) shows the variations of free volume with rise in concentration and temperature.
The internal pressure is a unique parameter which includes all types of the molecular interactions [**19**] .It is observed that from the Fig. 2(d) internal pressure increases with rise in concentration which supports the facts shown by the other evaluated parameters. It is defined as the force per unit area between the components.

Fig. 2(e) shows that acoustic impedance increases with rise in temperature and concentration. The increase in acoustic impedance indicates the change in elastic and inertial properties of the solution. This confirms the strong association between solute and solvent molecules [**20**].

Relaxation time is another important parameter to study the molecular aggregation in solution. Fig 2(f) shows that the relaxation time increases with concentration but decreases with rise in temperature. Decrease in Relaxation time with increase in temperature indicates the weakening of hydrogen bonding in the present system [**21**].

The molar sound velocity (R) increases with increase in concentration of the solute percentage almost linearly (Fig. 2(g)). This probably indicates that the relative association in the solution reinforces rather uniformly with increase in solute concentration [**22**]. The similar variations of Rao's constant were earlier reported [**23**].

Fig. 2(h) represents the variation of Gibb's free energy with rise in temperature and concentration. This trend of variation confirms the existence of strong hydrogen bonding between solute-solvent molecules.

APPLICATION

The measured and derived physical parameters data obtained in the present investigation is helpful for understanding the molecular interactions of N-1-naphthyl ethylene diamine dihydrochloride in aqueous medium as well as its physico-chemical and thermo dynamical properties. The present study provides better understanding of several biochemical and physiological processes. Using density viscosity and ultrasonic velocity the evaluated physical properties as a function of concentration and temperature plays key role in the development of molecular model, process design and operation in chemical engineering **[**24].

CONCLUSION

Acoustic and viscometric study was carried on aqueous N-1-Napththyl Ethylene diamine dihydrochloride of different concentration (0.001, 0.002, 0.003, 0.004 and 0.005) at 298.15 K and 300.15 K. These parameters were interpreted in connection with the molecular interactions in aqueous n-1-naphthyl ethylene diamine dihydrochloride solution. The experimentally obtained basic parameters density, viscosity and ultrasonic velocity and also the acoustic parameters in the present investigation indicates the nature type and strength of intermolecular interaction. In general we found that the molecular interaction increases with the addition of n-1-naphthyl ethylene diamine dihydrochloride solute in water. It is found that the linear variation in ultrasonic velocity some parameters confirms no complex formation present in understudied solute.

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