Thermodynamic Properties of Methylamine Hydrochloride in aqueous medium at 298.15K and 300.15K

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Abstract- The basic parameters such as ultrasonic velocity (v), Density (ρ) and Viscosity (η) of aqueous methylamine hydrochloride at different concentrations and temperature at 2MHz have been measured. These basic parameters have been used to evaluate various physical parameters such as Adiabatic compressibility (β), Acoustic impedance (Z), Free length (L_f), Free volume (V_f), Internal pressure (π_i), Molar volume (V_m), Relaxation time (τ), Rao's constant and Gibb's free energy (ΔG). The nature, strength and types of molecular interactions are discussed in terms of experimentally measured and derived parameters. The physico-chemical data obtained in the present investigation helps to study thermodynamic properties of aqueous solution of methylamine hydrochloride.

Keywords: molecular interactions, ultrasonic velocity, methylamine

1. INTRODUCTION

Different chemical engineering operations for the design of processes need the physical properties of pure amines and their mixtures with water. The physical properties of liquid, liquid mixtures can be studied by various techniques such as NMR, ESR, Raman spectroscopy, IR spectroscopy, ultrasonic and other dielectric methods [1]. But Ultrasonic technique is widely used as compared to other methods because it is easy to use, low cost and it shows spontaneous results. It is an important tool for examining the nature, strength and order of molecular interactions. The investigation of basic and derived physical parameters plays an important role to the study of intermolecular interactions in solutions [2-5] and also thermodynamic behaviour of solution. The understanding of molecular interactions has large contribution in different branches of science to measure and to predict the behaviour of physical and chemical processes which takes place in human body. In the present investigation, methylamine hydrochloride (CH_3NH_2HCl), molecular weight 67.52g/mol aqueous solution has been characterized in relation to basic parameters like ultrasonic velocity, density, viscosity and other derived parameters using ultrasonic technique. Using measured and evaluated parameters molecular interactions in this solution have been studied. The physical properties of the solution under present investigation are studied at temperature 298.15K and 300.15K in order to cover temperature range found in industrial application.

2. MATERIALS AND METHOD

In the present investigation, Methylamine Hydrochloride (CAS No. 593-51-1), having molecular weight 67.52 g/mol, minimum assay 99% was obtained from LOBA chemie India. The solvent double distilled water was used to prepare the fresh solution for different concentration. The ultrasonic velocity of the solutions was measured by using digital ultrasonic pulse echo velocity meter (VCT-70A) at frequency 2MHz with accuracy of 0.1%. The density of solution has been measured by using specific gravity bottle. An Ostwald viscometer is used to determine the viscosity of solution with high accuracy. The temperature controller was used to maintain the constant temperature during every measurement. The flow time of liquid in viscometer was measured by using electronic stop watch having high accuracy.

3. 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 is temperature 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)

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

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

4. RESULT AND DISCUSSION

The experimentally measured values of ultrasonic velocity, density and viscosity of aqueous methylamine hydrochloride solution of different concentration (0.1, 0.3, 0.5, 0.7, 0.9) mol/kg at different temperature 298.15K and 300.15K are as given in table1 whereas the values of derived physical parameters are in table 2.The variation of basic parameters are as shown in fig.(a-c) whereas derived parameters such as Adiabatic compressibility (β), Acoustic impedance (Z), Free length (L_F), Free volume (V_f), Internal pressure (π_i), Molar Sound velocity (R), Relative association (R_A), Relaxation time (τ) and Gibb's free energy (ΔG) verses concentration at temperature 298.15K and 300.15K are shown in fig.(d-l) respectively.

Table1. Measurement of ultrasonic velocity, density and viscosity of methylamine hydrochloride in aqueous medium at 298.15K and 300.15K.

Sr.No.	**(mol/kg)**	**u(m/s)**		**ρ(kg.m^{-3})**		**η(pa-s)**	
		298.15K	300.15K	298.15K	300.15K	298.15K	300.15K
1	0.1	1500.731	1503.144	996.433	966.003	0.958	0.929
2	0.3	1510.429	1513.485	1000.100	999.567	0.999	0.938
3	0.5	1520.870	1524.590	1002.036	1002.010	1.037	0.965
4	0.7	1531.457	1534.599	1004.481	1003.741	1.068	0.996
5	0.9	1541.557	1545.379	1006.926	1007.610	1.087	1.026

Table 2. Derived physical parameters of methylamine hydrochloride in aqueous medium at 298.15 K and 300.15K.

Sr.No.	**(mol/kg)**	**β 10^{-10}(N^{-1}m^2)**		**L_f 10^{-11}(m)**		**V_f 10^{-8}(m^3.mol^{-1})**	
		298.15K	300.15K	298.15K	300.15K	298.15K	300.15K
1	0.1	4.4560	4.4436	4.3422	4.3509	1.7036	1.7874
2	0.3	4.3828	4.3675	4.3064	4.3135	1.6392	1.8065
3	0.5	4.3145	4.2936	4.2727	4.2768	1.5887	1.7771
4	0.7	4.2447	4.2305	4.2380	4.2453	1.5579	1.7365
5	0.9	4.1791	4.1556	4.2051	4.2075	1.5538	1.7009

Sr.No.	(mol/kg)	π_i 10^9(pa)		Z 10^6(kg.m^{-2}s^{-1})		τ10^{-13}(s)	
		298.15K	300.15K	298.15K	300.15K	298.15K	300.15K
1	0.1	2.790	2.763	1.495378	1.497136	5.692	5.5061
2	0.3	2.814	2.742	1.510580	1.512829	5.838	5.4636
3	0.5	2.829	2.744	1.523966	1.527655	5.966	5.5229
4	0.7	2.834	2.751	1.538319	1.540340	6.044	5.6153
5	0.9	2.824	2.760	1.552233	1.557139	6.057	5.6845

Sr.No.	(mol/kg)	V_m10^{-5}(m^{3}mol^{-1})		R10^{-4}(m^{5}N^{-1})		ΔG10^{-21}(Jmol^{-1})	
		298.15K	300.15K	298.15K	300.15K	298.15K	300.15K
1	0.1	1.8154	1.8162	2.0784	2.0805	4.21213	4.1426
2	0.3	1.8265	1.8275	2.0957	2.0982	4.30511	4.1140
3	0.5	1.8406	1.8406	2.1166	2.1185	4.38441	4.1538
4	0.7	1.8535	1.8549	2.1365	2.1396	4.43263	4.2151
5	0.9	1.8663	1.8651	2.1559	2.1563	4.44017	4.2604

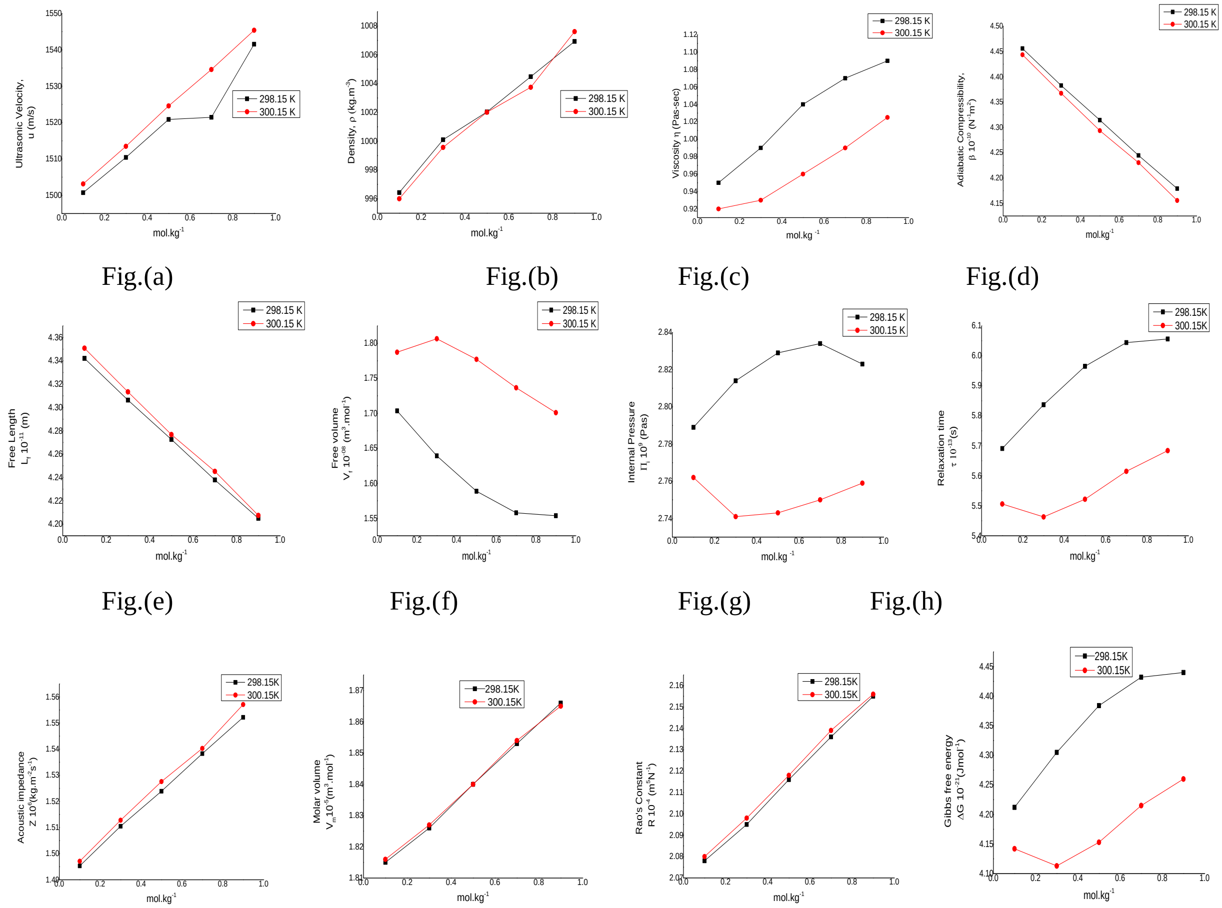

Fig.(a) Fig.(b) Fig.(c) Fig.(d)

Fig.(e) Fig.(f) Fig.(g) Fig.(h)

Fig.(i) Fig.(j) Fig.(k) Fig.(l)

Fig.1(*a-l*) variation of ultrasonic velocity (v), Density (ρ) and Viscosity (η) ,Adiabatic compressibility (β), Acoustic impedance (Z), Free length (L_f), Free volume (V_f), Internal pressure (π_i), Molar volume (V_m), Relaxation time (τ), Rao's constant and Gibb's free energy (ΔG) respectively of aqueous methylamine hydrochloride at different concentrations and temperature(298.15 to300.15)K.

The ultrasonic velocity of solution under investigation (fig. a) has been found to be increasing with increase in number of solute particles in solvent double distilled water and also with rise in temperature. The increase in ultrasonic velocity is an indication of enhanced solute-solvent molecular interaction and structure making tendency of solute methylamine hydrochloride in water. The linear variation of ultrasonic velocity with concentration shows absence of complex formation [6-7].The density variation has shown normal behaviour (fig. b) in the present investigation. Therefore density has no influence on the weakening or strengthening of cohesive forces. The opposition to flow is nothing but viscosity. A higher value of viscosity at higher concentration is clear indication of presence of large intermolecular forces and thus structure making tendency of solute in solvent. The rise in temperature increases the average kinetic energy of molecule which results in weakening of intermolecular forces and hence decreases in viscosity of the solution [8]. The change in adiabatic compressibility of solution with change in concentration and temperature occurs because electrostatic force between the components of solution makes structural changes in molecules. In the present study, it is found that adiabatic compressibility decreases with rise in concentration and temperature. The variation observed in adiabatic compressibility (fig.d) indicates the existence of solute-solvent interactions. Similar results have been reported by Giratkar et.al [9].Decrease in free length of the solution with rise in concentration indicates stronger cohesion leading to enhanced molecular aggregation where as increased free length with rise in temperature indicated weakening of cohesive forces [10, 11]. The structure making and breaking tendency of solute molecule [12] in solvent can be properly understood with the help of an important physical parameter free volume. The trend shown by this parameter with concentration and temperature in the present investigation supports the facts indicated by the parameters discussed earlier. Fig. (g) shows that internal pressure increases with increase in concentration, this type of variation might be due to increase of cohesive force and solute-solvent interaction in solution[13]. It indicates the formation of hydrogen bonding in between solute-solvent molecule. Decrease in internal pressure with rise in temperature reduces the solute- solvent interactions and [14].The acoustic impedance increases with both temperature as well as concentration. As $Z = \rho u$, with rise in concentration ρ and u increases therefore Z increases. Increase in Z occurs due to change in inertial and elastic properties of solution [15, 16]. It also shows that solute- solvent molecules are bounded with hydrogen bonding. Rao's constant increases with rise in temperature and concentration. It indicates the availability of more number of components in a given region of space. This leads to the tight packing of medium and thereby increased molecular interactions [17]. Gibb's free energy increases with increase in concentration. It indicates strong molecular aggregation through intermolecular hydrogen bonding [18]. Gibb's free energy decreases with increase in temperature. It shows that molecules are loosely packed due to weak interaction between solute-solvent molecules.

5. CONCLUSION

Acoustic and viscometric studies were carried on methylamine hydrochloride in aqueous solution of different concentrations (0.1, 0.3, 0.5, 0.7 and 0.9) mol/kg at temperature 298.15K and 300.15K. The variation in Physical parameters has shown the existence of molecular interactions. The solute-solvent interactions are predominant over other interactions. The physical parameter density has no influence on the association and disassociation.

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