IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 8, Issue 7 Ver. I (July. 2015), PP 81-86
www.iosrjournals.org

Thermo physical properties for the ternary systems 1,4-Bis(diphenylaminobenzene) (1) + Picric acid (2) + chloroform (3), at temperatures 298K, 303K and 308K

Shivani A. Thakur[*], Shubhajit Halder[†], Pratibha S. Agrawal[††]
[*]*Dr. Ira Nimdeokar P.G. and Research Centre for Chemistry, Hislop College, Nagpur-440001(M.S), India*
[†]*Department of Chemistry, Hislop College, Nagpur-440001(M.S), India*
[††]*Department of Applied Chemistry, Laxminarayan Institute of Technology, Nagpur-440033(M.S), India*

Abstract: *Density, speed of sound and viscosity for the ternary system formed by 1,4-Bis (diphenylaminobenzene)**,** picric acid and chloroform were measured at atmospheric pressure in the temperature range of 298K, 303K and 308K. The present investigation aims at the comparative study of stability constants of the "Acid-Amine" charge transfer complexes at three temperatures to gain a better understanding of the effect of temperature, and different structural aspects of acceptor-donor to the stability constants of charge transfer complexes under investigation. A quantitative relationship has been established among the thermodynamic properties like acoustical impedance (Z), sound velocity (U), Intermolecular free length (L_f), excess molar volume (V^E) and adiabatic compressibility (β) etc. The results obtained are much comparable and are in good agreement. A molecular interaction study has also been made successfully in the light of these acoustical properties.*

Keywords: *Charge transfer complexes, Acoustical properties, Stability constants, Viscosity, Intermolecular free length*

I. Introduction

In recent years, measurements of thermodynamic and transport properties of binary and ternary liquid mixtures have been adequately employed in understanding the nature of molecular systems and physico-chemical behaviour in liquid mixtures [1]. The viscosity of liquid mixtures is required in several calculations of engineering that involve fluid dynamic and heat and mass transference [2]. Ultrasonic investigations find extensive applications in predicting the physico-chemical behaviors and molecular interactions occurring in a variety of liquid mixtures. In a chemical industry, these properties are very significant in design calculations, heat transfer and mass transfer etc. There has been an increasing interest in the study of molecular interaction between the component molecules and they find applications in several industrial and technological processes. Ultrasonic is a non- destructive and quick method for the investigation of charge transfer complexes [3]. Further, such studies as a function of concentration are useful in gaining insight into the structure and bonding of associated molecular complexes and other molecular processes [4]. The carbonyl group has electron deficient carbons which can function as electrophiles. Basic groups like amino groups can interact with this group to form a complex and influence the properties of such compounds [5]. These studies are made mainly to investigate the effect of structure of donor molecules and polarity of medium on the stability of this type of complexes and the factor which plays significant role in the complexation [6]. In this study, viscosities and densities of the ternary system formed by 1,4-Bis(diphenylaminobenzene**)**, picric acid in chloroform solvent have been measured at the temperatures of 298K, 303K and 308K at atmospheric pressure. From these experimental data, the acoustical impedance (Z), intermolecular free length (L_f), excess molar volume (V^E) and adiabatic compressibility (β) have been calculated.

II. Experimental Method

All chemical agents used in this studywere Anal R grade. Densities, Viscosities and Ultrasonic Velocities were measured at 298K, 303K and 308K over a wide range of concentrations. The densities of pure compounds and their solutions were measured accurately using 10 ml specific gravity bottle in an electronic balance precisely and the accuracy in weighing is ± 0.1 mg. Viscosities of pure compounds and their mixtures were determined using Ostwald's Viscometer calibrated with double distilled water.

The ultrasonic velocity as measured by using variable path single crystal interferometer (Model F-81S, Mittal Enterprise, India) at fixed frequency 2 MHZ with accuracy of 0.03%. The temperature was maintained with an accuracy of 0.1^0C. Electronically digital operated constant temperature bath (Plasto Craft Industries) for low temperature bath Odel LTB-10 was used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature with accuracy in temperature

measurement -10^0C to -90^0C. Acoustical parameters such as adiabatic compressibility (β), free length (L_f), relaxation time (τ), stability constant (K) and the free energy change (ΔG^0_F) were calculated using standard equations.

Theory and calculations

The measured values of density (ρ) and ultrasonic velocity (u) were used to conclude various parameters.

$$\text{Viscosity } (\eta) = (at - b/t)\,\rho \quad (1)$$

Where a and b are the characteristic constants of the viscometer, ρ is the density and t represents the flow time.

$$\text{Adiabatic compressibility } (\beta) = 1/U^2\,\rho \quad (2)$$

$$\text{Free length } (L_f) = K\,\beta^{1/2} \quad (3)$$

Where K is temperature dependant constant

$$\text{Molar Volume } (V_m) = M\rho \quad (4)$$

Where M is mean molecular weight. It is calculated as ($M = X_1M_1 + X_2M_2+X_3M_3$) X_1, X_2 and X_3 are mole fractions and M_1, M_2 are molecular weights of constituent components of ternary liquid mixtures.

$$K = y/(c_2-y)^2 \quad (5)$$

K = Stability constant for complexation

$y = (c_2\,(k)^{1/2})]/[k - (k)^{1/2}]$

k is the ratio of deviation in the ultrasonic velocity values at concentrations c_1 and c_2 of the donor or acceptor from ideal value. This equation has been successfully used to determine the formation constant of several donor-acceptor complexes in solution [7,8].

The relaxation time is estimated from the following relation

$$\tau = 4/3\,\eta\beta \quad (6)$$

Knowing the viscosity of the liquid (η) and adiabatic compressibility (β), then τ can be calculated.

III. Results And Discussion

The measured values of ultrasonic velocity, density and viscosity at equimolar concentrations of acceptors and Picric acid (donor) in chloroform at 298K, 303K and 308K are given in Table 1. Amines behave as Lewis bases since they contain nitrogen as the basic centre with a lone pair of electrons. Carbonyl compounds contain a polar group in which electron deficient carbon can function as electron acceptor. Thus, donor-acceptor complexes can be formed between amine and carbonyl compounds. There are optical and ultrasonic methods to detect such complexes. In this article, we employed an ultrasonic method to detect these complexes. The stability constants (K) are determined from ultrasonic velocities and the trend in K values is explained on the basis of the structure of the carbonyl compounds. Picric acid is used as a donor in the formation of these types of complexes. Plots of ultrasonic velocity versus concentration at three temperatures are presented in Figure 1. Figure 2 contains similar plots for this system.

Table1. Ultrasonic velocity (m s^{-1}), Density (Kg m^{-3}) and Viscosity (10^{-3}Ns m^{-2}) values of 1,4-Bis(diphenylaminobenzene) with Picric acid in chloroform at 298K, 303K and 308K.

Equimolar Concentration	velocity(m s^{-1})	Density(Kg m^{-3})	Viscosity (10^{-3}Ns m^{-2})
298K			
0.03	1896.1	1458.0	1.472
0.06	1890.3	1463.8	1.458
0.09	1885.5	1469.6	1.460
0.12	1880.2	1475.4	1.455
0.15	1876.6	1481.2	1.448
0.18	1871.1	1487.0	1.444
0.21	1867.8	1492.8	1.432
0.24	1862.7	1498.6	1.426
0.27	1857.4	1504.4	1.421
0.30	1851.1	1510.2	1.409
303K			

0.03	1888.2	1446.2	1.430
0.06	1882.3	1452.0	1.426
0.09	1875.5	1459.8	1.416
0.12	1870.2	1465.0	1.404
0.15	1866.4	1472.2	1.402
0.18	1861.8	1479.4	1.389
0.21	1856.1	1485.6	1.382
0.24	1848.9	1492.8	1.377
0.27	1842.4	1498.0	1.363
0.30	1837.1	1505.2	1.362
308K			
0.03	1881.3	1438.2	1.433
0.06	1875.6	1445.2	1.419
0.09	1869.0	1451.5	1.406
0.12	1862.4	1458.7	1.416
0.15	1857.1	1464.2	1.408
0.18	1850.8	1471.3	1.401
0.21	1844.7	1477.2	1.392
0.24	1839.1	1485.6	1.389
0.27	1833.6	1492.5	1.378
0.30	1827.8	1499.1	1.365

It is seen from the Table 1 that ultrasonic velocity and viscosity decreases with concentration. The trend in the ultrasonic velocity with concentration indicates week interactions between 1, 4-Bis (diphenylaminobenzene) with Picric acid. Thus the complexation is concentration dependent.

From these values, various acoustical parameters like adiabatic compressibility, free length, and free volume have been evaluated and are presented in Table 2. The extent of decrease in adiabatic compressibility signifies the strength of molecular interaction. From Tables 2, it is observed that adiabatic compressibility, free length and free volume increase with increase in temperature and increase with increase in concentration of 1,4-Bis(diphenylaminobenzene) indicating the possibility of stronger interactions at higher concentration. Thus, the donor-acceptor complex formation between carbonyl compounds and 1,4-Bis(diphenylaminobenzene) is both concentration and structure-dependent.

Table 2. Adiabatic Compressibility ($10^{-11}m^2/N$), Intermolecular free length (pm) and molar volume ($10^6m^3mol^{-1}$) values of 1,4-Bis(diphenylaminobenzene) with Picric acid in chloroform at 298K, 303K and 308K.

Equimolar Concentration	β ($10^{-11}m^2$ /N)	L_f (pm)	V_m ($10^6m^3mol^{-1}$)
298K			
0.03	1.907	8.535	82.53
0.06	1.911	8.545	82.86
0.09	1.914	8.549	83.17
0.12	1.917	8.557	83.48
0.15	1.918	8.556	83.78
0.18	1.920	8.565	84.08
0.21	1.921	8.563	84.36
0.24	1.923	8.570	84.63
0.27	1.926	8.578	84.90
0.30	1.932	8.590	85.16
303K			
0.03	1.939	8.606	83.21
0.06	1.943	8.616	83.53
0.09	1.947	8.624	83.73
0.12	1.951	8.633	84.08
0.15	1.949	8.629	84.29
0.18	1.950	8.630	84.51
0.21	1.953	8.638	84.77
0.24	1.959	8.651	84.96
0.27	1.966	8.666	85.27
0.30	1.968	8.670	85.45
308K			
0.03	1.964	8.662	83.67
0.06	1.966	8.667	83.92
0.09	1.972	8.679	84.21
0.12	1.976	8.688	84.44

0.15	1.98	8.696	84.75
0.18	1.984	8.705	84.97
0.21	1.989	8.716	85.25
0.24	1.990	8.718	85.38
0.27	1.992	8.724	85.58
0.30	1.996	8.732	85.79

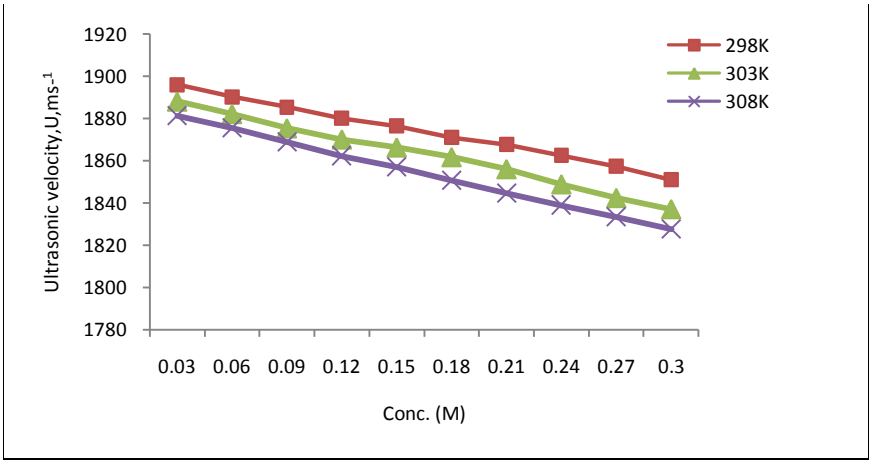

Figure 1. Plots of Ultrasonic velocity vs. concentration of 1,4-Bis(diphenylaminobenzene)-Picric acid

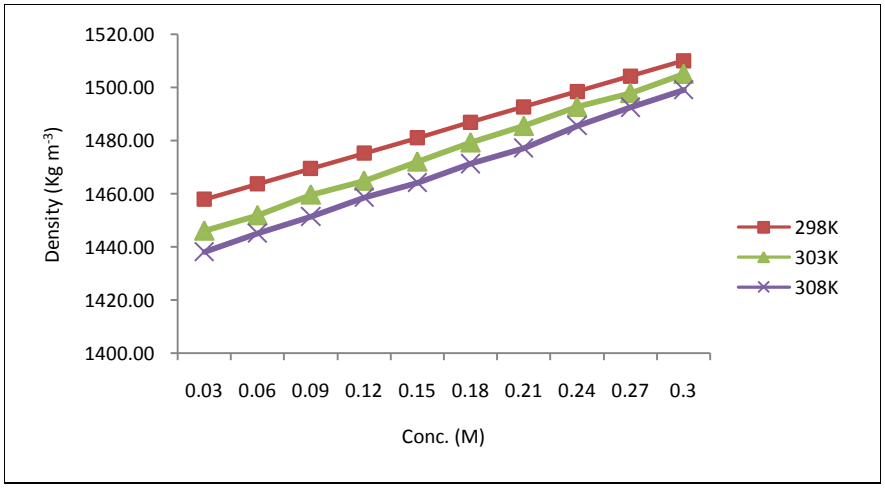

Figure 2. Plots of Density vs. concentration of 1,4-Bis(diphenylaminobenzene)-Picric acid**.**

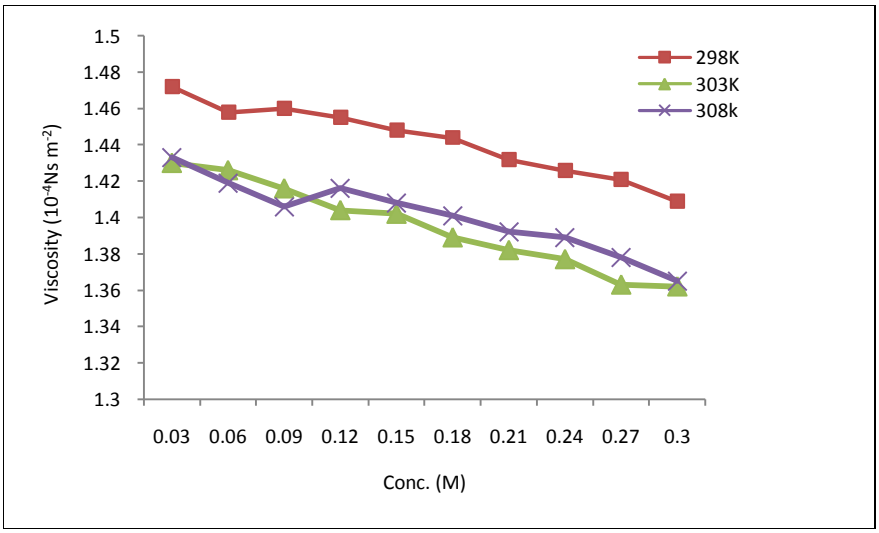

Figure 3. Plots of Viscosity vs. concentration of 1,4-Bis(diphenylaminobenzene)-Picric acid.

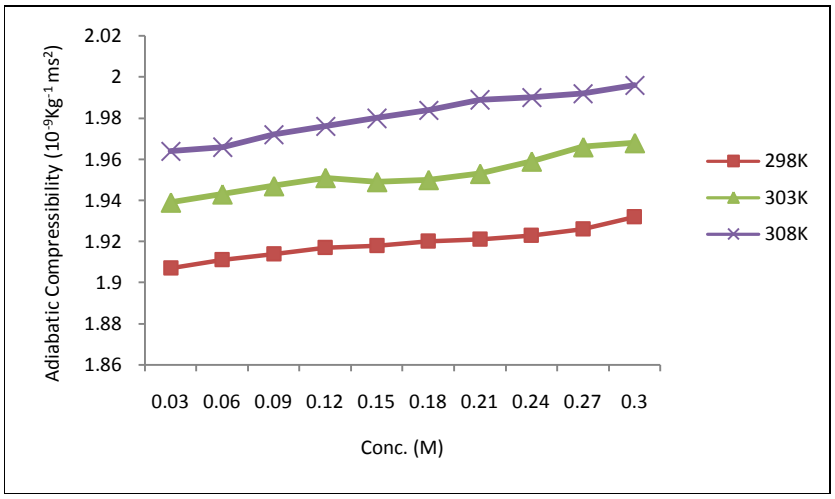

Figure 4. Plots of Adiabatic compressibility vs. concentration of 1,4-Bis(diphenylaminobenzene)-Picric acid.

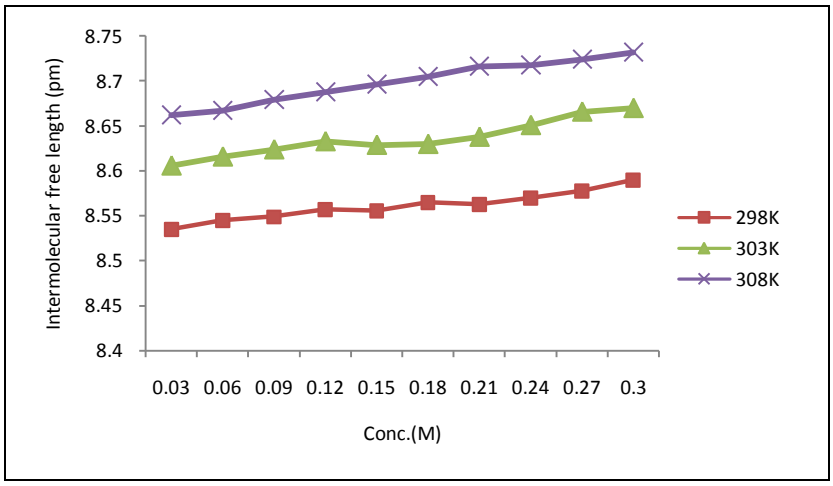

Figure 5. Plots of Intermolecular free length vs. concentration of 1,4-Bis(diphenylaminobenzene)-Picric acid.

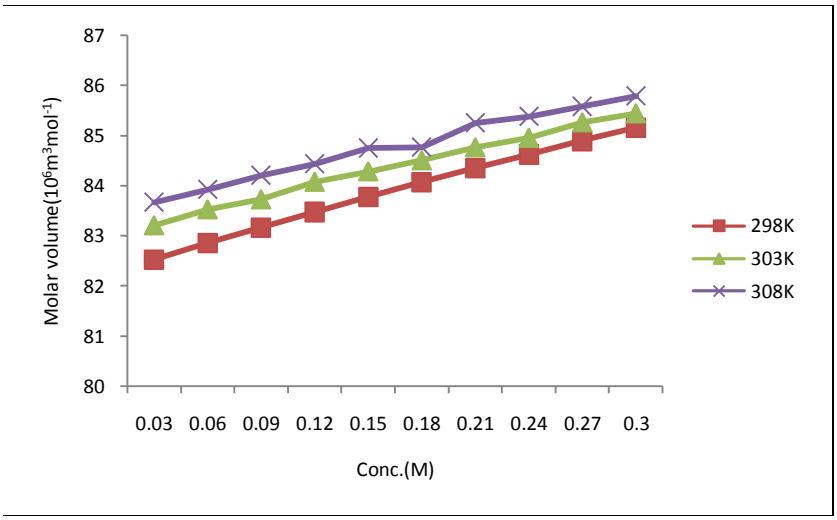

Figure 6. Plots of Molar volume vs. concentration of 1,4-Bis(diphenylaminobenzene)-Picric acid.

The formation constant can be used to compare stabilities of the charge transfer complexes [9-11]. From the values of formation constant, stability of the charge transfer complexes at 298K is more compare to 303K and 308K. The negative free energy of formation (ΔG^0_F) value for all complexes indicates that the donor-

acceptor complexes formed between acids and amines are thermodynamically stable. From Table 3, it is observed that the relaxation time (τ) decrease with rise of temperature.The relaxation time which is the order of 10^{-12} seconds is due to structural relaxation process **[**12**]** and such situation suggests that the molecules getrearranged due to cooperation process **[**13**]**. The Gibbs free energy (ΔG*) from Table 3 increases with increase of temperature. The increasing positive values of Gibbs free energy suggest that the closer approach of unlike molecules is due to hydrogen bonding **[**14,15**]**.

Table 3. Formation constant, free energy of formation, mean free energy of activation and mean viscous relaxation time values 1, 4-Bis (diphenylaminobenzene) with Picric acid in chloroform at 298K, 303K and 308K.

Temperature	K (M^{-1})	ΔG^0_F (kJ mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})	τ (10^{-13}) s
298K	2.84	-6.32	2.05	3.69
303K	2.77	-6.34	2.09	3.63
308K	2.74	-6.41	2.21	3.60

IV. Conclusion

Acids with electron-deficient carbonyl carbon form thermodynamically stable charge transfer complexes with electron donor amines. The complexation between acid and amine can be detected by ultrasonic method. The stabilities of these complexes depend on the structure of acceptor molecule and concentration of the donor-acceptors.

References

[1]. Prasanna Pradhan and Mahendra Nath Roy, Physics and Chemistry of Liquids, 52 (2014) 100.
[2]. Salvador Canzonieri, Alberto Camacho, Ruben Tabarrozzi, Miguel Postigob and LeliaMussari, Physics and Chemistry of Liquids, 50(4) (2012) 530.
[3]. Shubhajit Halder, ShivaniTomar, Pratibha S. Agrawal and Lalitmohan J. Paliwalc, Der Pharma Chemica, 5(6) (2013) 282.
[4]. V Kannappan, S J Askar Ali and P. A. Abdul Mahaboob, Indian J.Pure Appl.Phys.47 (2009) 97.
[5]. T.W.GrahamSolomons and Fryhle,Organic Chemistry,7th ed(John Wiley & Sons,Inc.,New York, 1088 (2002).
[6]. V Kannappan, G Hemalatha, Indian J.Pure Appl.Phys.43, 849 (2005).
[7]. S. Jayakumar, N. Karunanidhi, V. Kannappan.Indian J. Pure and Appl. Phys., 34 (1996) 761.
[8]. S. Kothai, Ph.D. Thesis, University of Madras, Chennai, India, (2003).
[9]. S.Mahendran, Ph.D.Thesis,University of Madras, India, (2002).
[10]. Shubhajit Halder, Pratibha S. Agrawal, Shivani A. Thakur and Lalitmohan J. Paliwal, IOSR Journal of Applied Chemistry, 7 (2014) 36.
[11]. V.Kannappan, R.Jayashanthi and E.J.P.Malar, Phys.Chem.liq. 40 (2002) 507.
[12]. E Kinser, A R Fray, Fundamentals of acoustics, wisely eastern, New Delhi, (1989).
[13]. A Ali, S Hydar, Nain. Adibas,J Chinese chem soc., 51 (2004) 477.
[14]. B Shipra, O Swati, Studies of some acoustical properties in binary solutions. Fluid phase Equilibaria, 178 (2001) 233.
[15]. Shubhajit Halder, Pratibha S. Agrawal, Shivani A. Thakur and Lalitmohan J. Paliwal, J. of Chem. & Pharm. Research, 6 (2014) 241.