Intermolecular Interaction between Chlorpheniramine and1-Ethanol at various Temperatures

SAMPANDAM ELANGOVAN[1]*, TILAHUN DIRIBA GARBI[2] and PONNUSAMY THILLAIARASU[3]

[1,2]Department of Physics, College of Natural and Computational Science, Wollega University, Nekemte, Ethiopia.
[3]Department of Chemistry, College of Natural and Computational Science, Wollega University, Nekemte, Ethiopia.

Abstract

Density (ρ), viscosity (η) and ultrasonic velocity (U) of chlorpheniramine with 1-ethanol mixtures are measured in a range of temperatures 303K, 308K and 313K. By using the systematic measurements, various physico chemical quantities, adiabatic compressibility (β), free length (L_f), free volume (V_f), viscous relaxation time (τ) and Gibbs free energy (ΔG) are attained. The deviations of those quantities to their ideal values are derived and revealed with the intermolecular interactions. The standard deviations and the coefficients of Redlich Kister polynomials of excess quantities are also determined to validate the calculations. From these observations, the existence of intermolecular interaction is confirmed and the strength of interactions with the temperatures as 303K>308K>313 K.

Introduction

Ultrasonic techniques are taking a vital role in the studies about molecular interactions between the solute and solvent systems at various temperatures.[1-3] The variations in the ultrasonic velocity with the density and viscosity of the solutions in a range of concentrations and temperatures of the liquid systems are useful to analyse various kinds of intermolecular forces acting on the molecules in the solutions.[4-6] Moreover, the changes in the adiabatic compressibility, free length, free volume, viscous relaxation time, Gibb's free energy and their excess values are supported to analyse the type of the molecular interactions subsist in the system. Chlorpheniramine is one of the pharmaceutical important amine group compounds. It is used in the treatment of allergic rhinitis and the common cold. 1-ethanol has a self-association and polar nature.

It acts as a proton donor in the mixture.[7] This research work elucidates the intermolecular interaction between the chlorpheniramine and 1-ethanol at 303K, 308K and 313K.

Materials and Methods
By using the mole fraction method, concentrations of liquid mixtures are prepared. The airtight standard measuring flasks are used to hold the solutions. A digital electronic mass balance (ACMAS-78094L, India) with the uncertainty of ±1mg is used to determine the mass of the liquids. Standard weights are used to calibrate the balance. Ostwald's viscometer is used to determine the viscosity of the solution with an uncertainty of ± 0.001 Nsm^{-2}.

Specific gravity bottles are used to measure the density of the solution with the accuracy of ±0.01 kg m^{-3}. The experimental errors in the measurement are avoided by repeating the measurements with standard liquids. An ultrasonic interferometer with a single frequency 2 MHz is used to observe the ultrasonic velocity of the solutions with ±1 ms^{-1} accuracy. Analytical Grades of chlorpheniramine and 1- ethanol are used with standard purification methods. The various physico chemical quantities are determined by using standard relations which are reported in the literature.[8-11] In the entire mixtures, x_1 and x_2 have represented the mole fraction of chlorpheniramine and 1-ethanol respectively.

Table 1: Physico chemical quantities of chlorpheniramine and 1-ethanol at various temperatures

x^1	ρ (kgm^{-3})	η × 10^{-3} (Nsm^{-2})	U (ms^{-1})	β ×10^{-10} (m^{2}N^{-1})	L_f ×10^{-10} (m)	V_f ×10^{-8} (m^{3}mol^{-1})	τ × 10^{-12} (s)	ΔG × 10^{-20} (KJmol^{-1})
T=303K								
0.0000	784.4	0.9675	1144	9.7411	0.6476	0.6755	1.2566	0.8658
0.0892	803.2	1.0099	1170	9.0974	0.6259	0.7351	1.2250	0.8509
0.1938	824.5	1.0584	1201	8.4147	0.6019	0.8079	1.1875	0.8343
0.3012	849.4	1.1146	1235	7.7189	0.5765	0.8976	1.1472	0.8153
0.3957	878.5	1.1805	1276	6.9891	0.5486	1.0093	1.1000	0.7940
0.5028	912.9	1.2584	1324	6.2478	0.5187	1.1508	1.0483	0.7695
0.6128	954.4	1.3524	1383	5.4815	0.4858	1.3337	0.9884	0.7410
0.7685	1005.4	1.4678	1454	4.7020	0.4499	1.5753	0.9202	0.7077
0.8046	1069.5	1.6131	1544	3.9196	0.4108	1.9042	0.8430	0.6679
0.9083	1152.6	1.8013	1661	3.1432	0.3679	2.3679	0.7549	0.6197
1.0000	1264.7	2.0550	1819	2.3909	0.3209	3.0544	0.6551	0.5596
T=308K								
0.0000	779.8	0.9382	1123	10.1685	0.6677	0.6880	1.2720	0.8922
0.0892	798.5	0.9872	1149	9.4799	0.6447	0.7554	1.2478	0.8762
0.1938	819.8	1.0433	1179	8.7819	0.6205	0.8376	1.2216	0.8584
0.3012	844.5	1.1082	1213	8.0548	0.5942	0.9388	1.1902	0.8383
0.3957	873.4	1.1843	1253	7.2923	0.5654	1.0649	1.1515	0.8153
0.5028	907.7	1.2744	1300	6.5178	0.5345	1.2247	1.1075	0.7891
0.6128	949.0	1.3829	1358	5.7175	0.5006	1.4310	1.0542	0.7587
0.7685	999.7	1.5163	1428	4.9035	0.4636	1.7033	0.9913	0.7230
0.8046	1063.6	1.6842	1517	4.0867	0.4233	2.0742	0.9177	0.6805
0.9083	1146.3	1.9017	1632	3.2764	0.3796	2.5973	0.8307	0.6289
1.0000	1257.9	2.1949	1786	2.4916	0.3305	3.3720	0.7291	0.5647

T=313K

0.0000	774.5	0.8938	1109	10.4981	0.6845	0.7261	1.2511	0.9065
0.0892	793.1	0.9516	1134	9.8027	0.6614	0.8041	1.2437	0.8896
0.1938	814.3	1.0177	1164	9.0652	0.6362	0.8987	1.2300	0.8707
0.3012	838.8	1.0942	1197	8.3139	0.6091	1.0156	1.2129	0.8493
0.3957	867.6	1.1839	1237	7.5261	0.5795	1.1613	1.1882	0.8250
0.5028	901.7	1.2900	1284	6.7261	0.5479	1.3456	1.1569	0.7972
0.6128	942.8	1.4180	1341	5.8995	0.5131	1.5838	1.1153	0.7650
0.7685	993.3	1.5752	1411	5.0589	0.4751	1.8980	1.0624	0.7273
0.8046	1056.8	1.7730	1498	4.2155	0.4337	2.3259	0.9965	0.6822
0.9083	1139.1	2.0294	1611	3.3830	0.3886	2.9294	0.9154	0.6276
1.0000	1250.1	2.3750	1765	2.5692	0.3386	3.8227	0.8135	0.5596
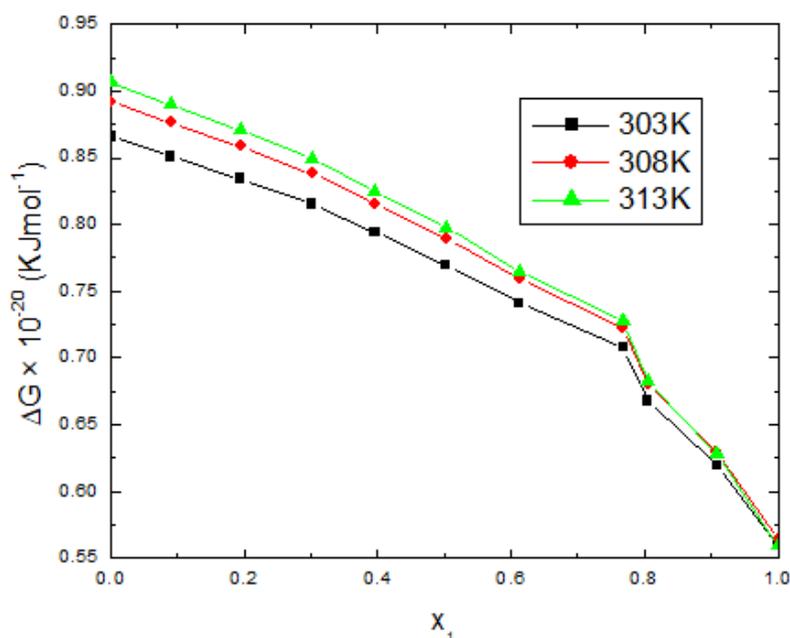
Fig. 1: Gibbs free energy variation with the mole fraction of chlorpheniramine and 1- ethanol at 303K,308K and 313K

Results and Discussions

Density (ρ), viscosity (η) and ultrasonic velocity (U) of chlorpheniramine and 1-ethanol are measured in a range of temperatures 303K, 308K and 313K. By using the observations, adiabatic compressibility (β), free length (L_f), free volume (V_f), viscous relaxation time (τ) and Gibbs free energy (ΔG) are determined and listed in Table 1. The density (ρ) of the solution increases with an increasing mole fraction of chlorpheniramine and it decreased in the 1-ethanol rich concentrations. While increasing the 1-ethanol the cluster packing ruptured and starts dissociation with increasing temperature of the concentrations. Similarly, viscosity (η) increases proportionally with the chlorpheniramine. While increasing the temperature of the liquid system, the cohesive forces acting in the mixture decreased. In general, ultrasonic wavelength varies physico chemical properties of a system.[12] Here, ultrasonic velocity decreases with raising the temperature

and chlorpheniramine concentrations. This trend revealed that the existence of intermolecular forces acting between the molecules and hydrogen bonds formed between the N-H group of chlorpheniramine and O-H group of 1-ethanol. However, the reverse trend is observed in the adiabatic compressibility (β) of the solutions with the increasing chlorpheniramine molecules and the experimental temperature. Furthermore, the free length (L_f) of the system increased with the concentration of 1-ethanol. This observation suggested that the dissociation of the system increases with increasing temperature. In this present work, the viscous relaxation time (τ) decreased with increasing temperature at the entire compositions of the mixture. This trend of the change in viscous relaxation time is due to the molecular dissociations. The variations in the Gibbs free energy with the mole fraction of chlorpheniramine are plotted in Fig1. The change in the Gibbs free energy due to the corresponding variation takes place in the inertial and elastic properties of the solution.[13-15]

Furthermore, the considerable variations in the quantities confirm the formation of weak hydrogen bonding in the liquid system. These changes in these parameters due to (i) Dissociation of molecules in the solution with the concentration of 1-ethanol (ii) Weak hydrogen bonding interactions in the mixture. The deviations of the quantities from their ideal values are useful to validate the observations and analyse the types of intermolecular forces acting between the molecules. It is reported that (i) Dispersion forces acting on the molecules lead to the positive sign in the corresponding excess values. (ii) Hydrogen bonding formation in the functional group of the solution signifies that the negative excess parameters.[16-19] The excess adiabatic compressibility (β^E), excess free length (L_f^E), excess free volume (V_f^E), excess viscous relaxation time (τ^E), excess Gibbs free energy (ΔG^E) with the mole fraction of chlorpheniramine in the entire temperature ranges are as shown in the Table2.

Table 2: Excess quantities of chlorpheniramine and 1-ethanol at various temperatures

x^1	β^E $\times 10^{-10}$ (m^2N^{-1})	L_f^E $\times 10^{-10}$ (m)	V_f^E $\times 10^{-8}$ (m^3mol^{-1})	τ^E $\times 10^{-12}$ (s)	ΔG $\times 10^{-20}$ $(KJmol^{-1})$
T=303K					
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0892	-0.2735	-0.0605	-0.0934	-0.0304	-0.2735
0.1938	-0.5501	-0.1357	-0.2031	-0.0752	-0.5501
0.3012	-0.8076	-0.2088	-0.3123	-0.1180	-0.8076
0.3957	-1.0340	-0.2751	-0.4183	-0.1567	-1.0340
0.5028	-1.2116	-0.3309	-0.5138	-0.1884	-1.2116
0.6128	-1.3189	-0.3691	-0.5883	-0.2095	-1.3189
0.7685	-1.3208	-0.3798	-0.6238	-0.2134	-1.3208
0.8046	-1.1637	-0.3430	-0.5873	-0.1902	-1.1637
0.9083	-0.7649	-0.2286	-0.4166	-0.1233	-0.7649
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000
T=308K					
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0892	-0.2837	-0.0637	-0.1159	-0.0257	-0.2837
0.1938	-0.5693	-0.1406	-0.2484	-0.0657	-0.5693
0.3012	-0.8360	-0.2151	-0.3811	-0.1041	-0.8360
0.3957	-1.0697	-0.2831	-0.5091	-0.1387	-1.0697
0.5028	-1.2543	-0.3406	-0.6243	-0.1674	-1.2543
0.6128	-1.3656	-0.3807	-0.7146	-0.1864	-1.3656
0.7685	-1.3673	-0.3907	-0.7586	-0.1899	-1.3673

0.8046	-1.2044	-0.3522	-0.7151	-0.1689	-1.2044
0.9083	-0.7918	-0.2354	-0.5087	-0.1090	-0.7918
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000
T=313K					
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0892	-0.2938	-0.0658	-0.1417	-0.0217	-0.2938
0.1938	-0.5895	-0.1455	-0.3018	-0.0580	-0.5895
0.3012	-0.8645	-0.2222	-0.4607	-0.0926	-0.8645
0.3957	-1.1062	-0.2928	-0.6139	-0.1240	-1.1062
0.5028	-1.2960	-0.3521	-0.7526	-0.1497	-1.2960
0.6128	-1.4103	-0.3928	-0.8608	-0.1668	-1.4103
0.7685	-1.4107	-0.4021	-0.9134	-0.1697	-1.4107
0.8046	-1.2431	-0.3639	-0.8612	-0.1510	-1.2431
0.9083	-0.8170	-0.2435	-0.6130	-0.0969	-0.8170
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000
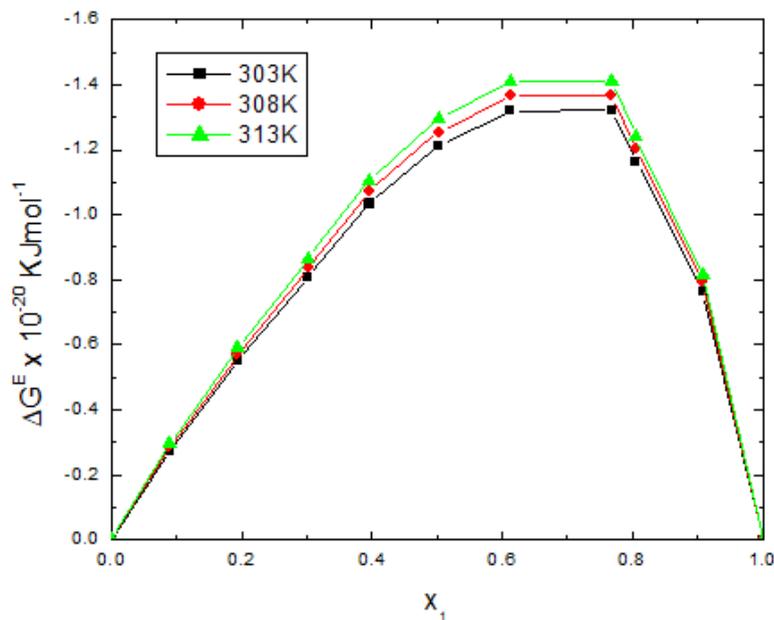
Fig. 2: Excess Gibbs free energy variation with the mole fraction of chlorpheniramine and 1- ethanol at 303K, 308K and 313K

In this work, all the parameters are shown negative excess values in the entire mole fractions of the liquid system. The negative excess adiabatic compressibility (β^E) increases with the concentrations of 1-ethanol, then decreasing due to the increasing number of dipoles due to the chlorpheniramine. Further, the negative excess free length (L_f^E) is increasing up to a mole fraction of $x_1 \sim 0.7$, decreased with increasing concentration of chlorpheniramine.

This may due to the increasing dissociation of molecular clusters. The changes in negative excess free volume (V_f^E) reveal that (i) Volume changes due to dipole-dipole interaction in the solution. (ii) Hydrogen bonding between the functional groups in the liquid system.[20] A polynomial variation in the negative excess viscous relaxation time (τ^E) is noticed with decreasing concentration of 1-ethanol. The excess Gibb's free energy (ΔG^E) variation with

the concentration of chlorpheniramine is plotted in Fig.2. The significant changes in the ΔG^E interpreted that increasing the molecules of 1-ethanol, rupture the hydrogen bonding formation between the hydroxyl and the amine groups in the liquid mixture. Moreover, these excess values are increased by raising the temperature from 303K to 313K. The standard deviations and Redlich–Kister's polynomial coefficients of the excess parameters are determined as in Table-3. The standard deviations are found within a minimum range and the determined Redlich coefficients have supported the validation of the excess parameters. Thus the observed physico chemical quantities and their excess values confirmed that the presence of hydrogen bonding interaction between the chlorpheniramine and 1-ethanol. Thus the strength of intermolecular interaction is observed in the order of 303K > 308K > 313K.

Table 3: Redlich-Kister coefficients and standard deviations of chlorpheniramine with1-ethanol at various temperatures

Parameters	Temperature (K)	a_0	a_1	a_2	σ
β^E	303	-0.4475	0.3345	-0.2071	0.0565
$\times 10^{-10}$ (m^2N^{-1})	308	-0.3175	-0.3055	-0.0895	0.0565
	313	-0.3175	0.4085	-0.0965	0.0565
L_f^E	303	-1.0035	0.4875	0.1865	0.0685
$\times 10^{-11}$ (m)	308	-0.7655	0.1835	0.2085	0.0555
	313	-1.1635	0.5265	0.3145	0.0695
V_f^E	303	-0.2485	-0.6185	0.5485	0.0575
$\times 10^{-8}$	308	-0.3025	-0.9985	0.9795	0.0635
(m^3mol^{-1})	313	-0.3345	-1.4565	1.4035	0.0715
τ^E	303	-0.0865	-0.1045	-0.1265	0.0545
$\times 10^{-12}$	308	-0.0205	-0.0825	-0.2135	0.0585
(s)	313	0.0335	-0.0275	-0.3225	0.0535
ΔG^E	303	-2.0275	1.1265	0.5765	0.0615
$\times 10^{-20}$	308	0.0885	0.4445	-0.8495	0.0545
$(KJmol^{-1})$	313	0.3385	-2.1395	-2.4175	0.0685

Conclusion

Various physicochemical parameters and the excess values of chlorpheniramine and 1-ethanol are determined at 303K, 308K and 313K. Redlich coefficients of the excess polynomial curve and the standard deviations of the data are also reported. The experimental observations and theoretical calculations confirmed that the existence of intermolecular interaction between the selected binary system. Based on the observations, the strength of intermolecular interaction between chlorpheniramine and 1-ethanol is obtained in the order of 303K>308K>313 K.

Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this article.

References

1. L. Palaniappan and S.Nithyanantham, Molecular interactions from the experimental and validation with estimated theoretical sound velocity. *Chemistry Africa*. 3, 277-285 (2020).

2. B. Mukesh, T. Sreekanth, M. Gowrisankar and M. Raveendra, Study of intermolecular interactions in binary mixtures of 2 methoxyaniline with chlorinated ethanes at various temperatures. *J. Sol. Chem.*49, 1337-1356 (2019).

3. H. Li, C. Song, L. Xu and G.Liu, Intermolecular Interactions in 1,6-Diaminohexane + Water Mixtures at 293.15 to 333.15 K, *Russ J. Phys Chem*, 94, 1356–1362 (2020).

4. S. Beebi, S.M. Nayeem and C. Rambabu, Investigation of molecular interactions in binary mixture of dimethyl carbonate + N-methylformamide at T = (303.15, 308.15, 313.15 and 318.15) K. *J. Therm Anal Calorim.* 135, 3387–3399 (2019).

5. S. Vani Latha, G. Little Flower, K. Rayapa Reddy, C.V.N Rao and A. Ratnakar, Densities, ultrasonic velocities, excess properties and IR spectra of binary liquid mixtures of organic esters (ethyl lactate, some organic carbonates). *J. Sol. Chem.* 46, 305–330 (2017).

6. H. Wang, Theoretical study on the molecular structure, intermolecular interaction and spectral features of 2-aminopyridine/ 2,3-dichloro-5,6-dicyano-1,4-benzoquinone complex. *J. Chem Sci.* 129, 775–782 (2017).

7. S. Elangovan and S. Mullainathan, Intermolecular interactions in methyl formate– ethanol mixtures at 303–313 K according to ultrasonic data. *Russ J. Phys Chem.* 88, 601-606 (2014).

8. F. S. Mjalli and O. U. Ahmed, Characteristics and intermolecular interaction of eutectic binary mixtures: Reline and Glyceline. *Korean J. Chem. Eng.* 33, 337–343 (2016).

9. V.V. Kompaneets and I.A.Vasileva, The influence of terminal substituents of diphenylbutadiene on the parameters of intra- and intermolecular interactions. *Opt. Spectrosc.* 122, 615–624 (2017).

10. H. Eyring and J. F.Kincaid, Free volumes and free angle ratios of molecules in liquids. *J. Chem Phys.* 6, 620-629 (1938).

11. O. Redlich and A. T. Kister, Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng Chem.* 40, 345-348 (1948).

12. V. Vanathi, S. Mullainathan and S. Nithyanantham, Acoustical parameters of toluene + chloroform + cyclohexane mixtures at 303.15, 308.15 and 313.15K. Russian. *J. Phys. Chem.* 86, 1204-1207 (2012).

13. M.K.M.Z. Hyder, S. Akhtar, S.H. Mir and A. Khosla, Density, excess molar volume and some of their derived properties of the binary systems of methyl acetate with methyl derivatives of monoethanolamine between 293.15 and 313.15 *K. Microsyst Technol.* 24, 4357–4371 (2018).

14. S. Elangovan and D.W. Amente, Intermolecular Interaction of Methyl Formate with 1-butanol, 1-pentanol and 1-hexanol at 303K. *Material. Sci. Res.* India.14, 212-214 (2017).

15. H. Iloukhani and M.Soleimani, Measurement and modeling the excess molar volumes and refractive index deviations of binary mixtures of 2-propanol, 2-butanol and 2- pentanol with n-propylamine. *J. Sol. Chem.* 46, 2135–2158 (2017).

16. D. Ma, Q. Liu, C. Zhu, H. Feng and Y. Ma, Volumetric and viscometric properties of ternary solution of (N-methyldiethanolamine + monoethanolamine + ethanol). *J. Chem. Thermodyn.* 134, 5-19 (2019).

17. R. J. Fort and W. R. Moore, Viscosities of binary liquid mixtures. Trans. *Faraday Soc.* 62, 1112-1119 (1966).

18. P. Droliya and A. K. Nain, Densities, ultrasonic speeds, excess and partial molar properties of binary mixtures of acetonitrile with some alkyle methacrylates at temperatures from 293.15K to 318.15K. *J. Chem. Thermodyn.*123,146-157(2018).

19. P. Vasundhara, M. Raveendra, C. Narasimharao, N. V. Reddy, K. S. Kumar and P. Venkateswaralu, Effect of Arrhenius energy factor on molecular interactions of binary liquid mixtures, *J. Therm Anal Calorim*. 135, 2541–2564 (2019).

20. S.Pradhan and S. Mishra, A thermodynamic investigation of solute - solvent interactions through volumetric, ultrasonic, dielectric, refractive and excess properties of binary mixtures of Tri-n-butyl phosphate with dichloro, trichloro and tetrachloromethane at 298.15 K. *J. Mol. Liq.*2791, 561-570 (2019).