Volume : 2 | Issue : 9 | September 2013 • ISSN No 2277 - 8179

Research Paper

Measurement of Some Thermodynamic and Acoustic Properties of 1-Alkanols in Butylacetate with Cyclohexane at Different Temperatures

Physics

KEYWORDS : Adiabatic compressibility, free length, Gibbs free energy, dispersive force, molecular interaction

T. Sumathi — Department of Physics, DDE, Annamalai University, Annamalainagar – 608 002, Tamilnadu, India.

U. Gnanasheela — Department of Physics, DDE, Annamalai University, Annamalainagar – 608 002, Tamilnadu, India.

ABSTRACT

In this work, densities (ρ), speed of sound (U) and viscosities (η) have been measured over the whole composition range for the binary mixtures of n-butyl acetate and cyclohexane with 1-propanol, 1-butanol, 1-pentanol and 1-hexanol. From these data, acoustical parameters such as adiabatic compressibility (β), free length (L_f), Gibbs free energy (ΔG), excess adiabatic compressibility (β^E), excess free length (L_f^E), excess viscosity (η^E) and excess velocity (U^E) have been estimated using the standard relations. The variation of these properties with composition and temperature are discussed in terms of molecular interactions between unlike molecules of the mixtures.

Introduction

Ultrasonic study is a subject of extensive research and finds its usefulness in the fields of biology, bio-chemistry, dentistry, engineering, geography, geology, medicine, polymers industry etc. Study of molecular interactions in organic liquid mixtures by measuring the ultrasonic velocity is of great interest. The measurement of ultrasonic velocity have been adequately employed in understanding the nature of molecular systems and physico-chemical behaviour in liquid mixtures (Kumara Sastry *et al.*, 2012). In recent years, there has been considerable advancement in the experimental investigation of excess thermodynamic properties of liquid mixtures. These properties have been adequately employed in understanding the nature of molecular interactions in binary and ternary liquid mixtures (Radhamma *et al.*, 2008). Several theoretical contributions have been routinely used to calculate the excess properties of liquid mixtures using the experimental data, such as density, viscosity and velocity of pure liquids and their ternary mixtures over the whole composition range at a particular temperature or several temperatures are useful for a full understanding of their thermodynamic and transport properties as well as for practical chemical engineering purposes (Mahendra Nath Roy *et al.*, 2007). The compositional dependence of thermodynamic properties has proved to be a very useful tool in understanding the nature and extent of pattern of molecular aggregation resulting from inter-molecular interaction between components (Sathyanarayana *et al.*, 2002).

For a better understanding of a physico-chemical properties and the molecular interactions between the participating components of these mixtures ultrasonic velocities and densities are measured at 303, 308 and 313K over entire concentration range. Various thermodynamic parameters like adiabatic compressibility (β), free length (L_f), Gibbs free energy (ΔG), excess adiabatic compressibility (β^E), excess free length (L_f^E), excess viscosity (η^E) and excess velocity (U^E) were also been evaluated. The variations of these parameters with composition of the mixtures are discussed in terms of molecular interactions.

Materials and methods

The chemicals used in the present work were Analytical Reagent (AR) grade with minimum assay of 99.9% were obtained from Sd fine chemicals India, which are used as such without further purification. Water used in the experimental data was deionised, distilled and degassed prior to making solutions. The density was determined using a specific gravity bottle by relative measurement method with an accuracy of ± 0.01 kgm^{-3}. The purities of the above chemicals were checked by density (ρ) determination by pycnometer at 303, 308 and 313 K ± 0.1K which showed an accuracy of ± 0.1 mg on a electronic digital balance (model: SHIMADZU AX 200). The dynamic viscosities (η) were measured using Ostwald's viscometer (10 ml) calibrated with triple distilled water at all experimental temperatures. An electronic digital stopwatch with an accuracy of ± 0.01s was used for flow time measurement. The speed of sound waves were obtained by using ultrasonic interferometer (Mittal Enterprises, New Delhi) at a fixed frequency of 3 MHz with an accuracy of ± $2ms^{-1}$. An electronically digital operated constant temperature bath (RAAGA Industries, Madras-61) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. For preparing various concentration mixtures, the mole fraction of second component cyclohexane was kept constant (X_2=0.4) and the mole fractions of other two components were varied from 0.0 to 0.6.

Theory

The various acoustical parameters such as adiabatic compressibility (β), free length (L_f) and Gibbs free energy (ΔG) were determined using the following equations (Asghar *et al.*, 2010; Wankhede *et al.*, 2008; Kumara Sastry *et al.*, 2012; Savaroglu *et al.*, 2007);

$$\beta = \frac{1}{U^2\rho} \quad \ldots(1)$$

$$L_f = K_T\beta^{1/2} \quad \ldots(2)$$

$$\Delta G = kT \ln\left(\frac{kT\tau}{h}\right) \quad \ldots(3)$$

where, k is Boltzmann's constant, T absolute temperature. h the Planck's constant and τ the viscous relaxation time $\tau = \left(\frac{4}{3}\right)\eta\beta$

The excess parameters (A^E) such as excess adiabatic compressibility (β^E), excess free length (L_f^E), excess viscosity (η^E) and excess velocity (U^E) were computed by the relation;

$$A^E = A_{exp} - A_{id}$$

where

$$A_{id} = \sum_{i=1}^{n} A_i X_i \text{ , } A_i$$

is any acoustical parameter and Xi the mole fraction of the liquid component i.

Results and Discussion

From the Table 1 it is observed that in all the four systems the density decreases while the viscosity and ultrasonic velocity of the ternary liquid mixtures are increasing with increasing mole fraction of 1-alkanols. It is observed that as the number of hydrocarbon group or chain length of alcohol increases the sound velocity increases. However, in all the ternary systems the values of ultrasonic velocity, density and viscosity of alkanols decrease with increase in temperature.

Adiabatic compressibility (β) is a powerful thermodynamic parameter in sensing the molecular interactions in liquid mixtures

Volume : 2 | Issue : 9 | September 2013 • ISSN No 2277 - 8179

(Anwar Ali *et al.*, 2006). Adiabatic compressibility (β) is found to be decreased with increasing concentration of alcohols.

The deviation in adiabatic compressibility can be explained by taking into consideration of the following factor.

1. Loss of dipolar association and difference in size and shape of the component molecules leads to decrease in velocity and increase in compressibility.

2. Dipole-dipole interaction or hydrogen bonded complex formation between unlike molecules leads to increase in sound velocity and decrease of compressibility. The actual deviation depends on the resultant effect (Ravichandran and Ramanathan, 2010).

It is primarily the compressibility that changes with structure which leads to change in ultrasonic velocity. The change in adiabatic compressibility in liquid mixtures indicates there is a definite contraction on mixing and the variation may be due to complex formation (Asghar *et al.*, 2010). The decrease in adiabatic compressibility suggests that there is significant interaction between unlike molecules (Praharaj *et al.*, 2012).

It is observed from the Table 2 the free length (L_f) decreases with increase in mole fraction of 1-alkanols. Intermolecular free length is found to be a predominating factor which depends upon adiabatic compressibility and shows a similar behaviour as that of compressibility. According to the Eyring Kincaid (1938) model for sound propagation, ultrasonic velocity increases as intermolecular free length decreases in the liquid mixture and vice versa. Therefore, intermolecular free length is one of the important factors for deciding the nature of change in acoustic parameters in the liquid mixture (Dash Ashok Kumar and Paikaray Rita, 2013). The increase in velocity and decrease in compressibility and free length with increase in mole fraction of 1-alkanols indicates significant interaction between the mixture (Wankhede *et al.*, 2008) and the order of the interaction for β and Lf is 1-propanol > 1-butanol>1-pentanol>1hexanol. Increase of β and Lf with temperature for all ternary mixtures suggest breaking of hetro and homo association of molecules at higher temperatures (Nikam *et al.*, 2000).

From the Table 2 it is observed that the Gibbs free energy ΔG increases with increase in concentration of 1-alkanols in all the systems. The increasing positive values of Gibb's function suggest that the closer approach of unlike molecules is due to hydrogen bonding. The increase in Gibbs free energy value confirms the availability of intermolecular interaction (Aravinth Raj et al., 2011). The increase in Gibbs energy with temperature in all the mixtures indicate the need for longer time for the cooperative process or the rearrangement of molecules in the mixtures (Ravindranatha Reddy *et al.*, 1995).

From the Figs. 1 and 2 it is observed that the excess adiabatic compressibility (β^E) and excess free length (L_f^E) are positive. The values of β^E, L_f^E depends upon several physical and / or chemical contributions. The physical contribution consists of dispersion forces or weak dipole – dipole interaction that leads to positive values β^E and L_f^E. Another factor, which involves a physical contribution, is the geometrical effect allowing the fitting of molecules of two different size into each other's structure resulting in negative β^E and L_f^E values.

Mixing of butyl acetate with 1 – alkonols would induce dissociation of the hydrogen – bonded structures present in pure alkanols with subsequent formation of H – bonds between oxygen atoms of butylacetate and hydrogen atom of hydroxyl group of 1 – alkanol molecules. The positive values of β^E and L_f^E indicate weak interactions between the components of the mixture (Anil Kumar Nain, 2013). The positive values of β^E and L_f^E mean that the mixture is more compressible than the corresponding ideal mixture. Therefore, in this system, an expansion in free volume is considered to occur, making the mixtures more compressible than the ideal mixture, which ultimately culminates into the positive values of β^E and L_f^E (Iloukhani and Rostami, 2003).

The observed excess viscosities (η^E) are negative for all the systems over the concentration range investigated (Fig. 3). Positive values of ηE are indicative of strong interactions whereas negative values indicate weak interactions. The observed negative deviations in viscosity support the main factor of breaking of the self associated alcohols and weak interaction between unlike molecules (Gyan P.Dubey and Monika Sharma, 2008). The negative deviations in the viscosity would also imply that (i) the mixture is less viscous than the corresponding ideal mixture and (ii) the weak dispersive interactions are operating in the system (Dubey *et al.*, 2010; Ali *et al.*, 1999). The negative values of viscosity deviation decreases in the following sequence; propanol > butanol > pentanol > hexanol.

From Fig. 4 it is observed that excess velocity (U^E) values are also negative for all the systems studied. Generally, negative values of U^E indicate dispersion forces due to weak interactions whereas positive values of UE indicate strong interactions. The observed negative values for the ternary mixtures reinforces that the dispersion forces are operating in the studied systems (Sreekanth *et al.*, 2012; Gokhan Savaroglu *et al.*, 2007).

CONCLUSION

In the present investigation the variation in the acoustic parameters, the sign and extent of deviation of the excess function derived from the ultrasonic velocity, density and viscosity suggest the presence of weak molecular interaction between the component of molecules in the ternary mixtures.

The observed positive values of β^E, and L_f^E and the negative of η^E and U^E in all the four systems reveals the presence of weak dipolar and dispersive interaction between the component molecules in the mixtures. It is concluded that, the strength of associative interaction between the unlike molecules weakens with the increase in chain length of the 1-alcohols and the order of interaction is as follows; 1-propanol > 1-butanol > 1-pentanol > 1-hexanol i.e., interaction decrease with increase in alkyl chain length in 1-alkanol molecules, probably due to less proton donating tendency to higher alcohols.

Table 1
Values of Density (ρ), Viscosity (η) and Velocity (U)

Mole fraction		ρ/(kgm^{-3})			η/(×10^{-3} Nsm^{-2})			U/(ms^{-1})		
	Temperature (K)				Temperature (K)		Temperature (K)			
X_1	X_3	303	308	313	303	308	313	303	308	313
Propanol + Cyclohexane + n-butyl acetate of system I										
0.0000	0.5999	827.18	822.00	818.96	0.6221	0.5968	0.5585	1148.65	1129.34	1112.65
0.1000	0.5000	817.92	815.76	813.53	0.6353	0.6049	0.5671	1155.94	1134.48	1116.94
0.1999	0.4000	812.96	811.15	809.43	0.6436	0.6115	0.5800	1159.68	1139.67	1120.43
0.3000	0.3000	808.98	806.12	803.56	0.6901	0.6404	0.6084	1163.04	1144.23	1124.87
0.4000	0.2000	802.95	800.62	795.99	0.7407	0.6938	0.6377	1167.54	1149.38	1130.54
0.5000	0.1000	799.76	794.98	789.99	0.8187	0.7779	0.7192	1170.60	1154.28	1134.99

0.6000	0.0000	788.65	783.64	780.93	1.0498	0.9670	0.8600	1179.65	1163.54	1142.85
Butanol + Cyclohexane + n-butyl acetate of system II										
0.1000	0.5000	813.45	807.34	804.12	0.6444	0.6047	0.5644	1159.34	1141.56	1118.64
0.2001	0.4000	809.54	803.67	800.88	0.6978	0.6653	0.6092	1162.98	1144.44	1125.93
0.2999	0.3000	803.89	799.75	798.97	0.7564	0.6893	0.6401	1167.20	1148.85	1128.93
0.4001	0.1999	799.67	794.83	792.65	0.8730	0.7747	0.7060	1170.80	1154.76	1134.24
0.4999	0.0999	791.65	788.65	785.42	0.9859	0.9171	0.8643	1177.44	1160.40	1141.68
0.6000	0.0000	783.87	779.54	773.45	1.2414	1.1318	1.0024	1192.44	1173.36	1152.28
Pentanol + Cyclohexane + n-butyl acetate of system III										
0.0999	0.4999	810.65	805.65	801.65	0.6650	0.6232	0.5872	1162.00	1143.60	1125.48
0.1995	0.4000	803.05	800.09	797.86	0.7045	0.6683	0.6196	1170.36	1148.16	1129.32
0.2998	0.3000	796.40	792.99	789.69	0.8066	0.7597	0.6942	1176.60	1156.44	1141.95
0.4000	0.2000	793.63	789.29	787.46	0.9322	0.8638	0.7957	1183.80	1164.72	1145.64
0.5000	0.1001	787.36	782.46	780.39	1.1734	1.0315	0.9053	1192.68	1180.32	1155.90
0.5992	0.0000	779.79	776.17	770.75	1.4856	1.3237	1.1494	1213.68	1195.08	1170.60
Hexanol + Cyclohexane + n-butyl acetate of system IV										
0.1001	0.5001	808.56	800.65	798.67	0.6716	0.6398	0.6033	1166.04	1146.36	1128.24
0.2000	0.4000	800.47	794.84	790.43	0.7961	0.7493	0.6848	1177.44	1159.68	1141.44
0.2999	0.2999	794.37	789.66	787.48	0.9342	0.8584	0.7888	1184.40	1168.56	1156.32
0.3999	0.1999	790.31	785.78	783.56	1.0956	1.0202	0.9063	1200.36	1178.70	1161.48
0.5000	0.1000	785.69	780.05	777.96	1.3912	1.2368	1.1439	1212.84	1196.28	1178.28
0.6000	0.0000	777.75	771.37	769.08	1.8536	1.6362	1.4813	1232.04	1212.84	1200.72

Table 2
Values of Adiabatic compressibility (β), Free length (L_f) and Gibbs free energy (ΔG*)

Mole fraction		β/(× 10^{-10} pa^{-1})		L_f/(× 10^{-10}m)			ΔG*/(× 10^{-20}) KJ mol^{-1}			
	Temperature (K)			Temperature (K)			Temperature (K)			
X_1	X_3	303	308	313	303	308	313	303	308	313
Propanol + Cyclohexane + n-butyl acetate of system I										
0.0000	0.5999	9.164	9.539	9.864	0.6040	0.6212	0.6376	0.6557	0.6730	0.6767
0.1000	0.5000	9.151	9.526	9.854	0.6036	0.6207	0.6373	0.6639	0.6781	0.6828
0.1999	0.4000	9.148	9.493	9.842	0.6035	0.6197	0.6369	0.6692	0.6812	0.6920
0.3000	0.3000	9.139	9.475	9.836	0.6032	0.6191	0.6367	0.6980	0.7001	0.7124
0.4000	0.2000	9.137	9.465	9.830	0.6031	0.6188	0.6366	0.7275	0.7337	0.7324
0.5000	0.1000	9.125	9.442	9.828	0.6027	0.6180	0.6365	0.7688	0.0781	0.7843
0.6000	0.0001	9.113	9.427	9.805	0.6023	0.6175	0.6357	0.8723	0.0873	0.8605
Butanol + Cyclohexane + n-butyl acetate of system II										
0.1000	0.5000	9.147	9.506	9.939	0.6035	0.6201	0.6400	0.6697	0.6771	0.6844
0.2001	0.4000	9.134	9.501	9.850	0.6030	0.6199	0.6372	0.7024	0.7174	0.7136
0.2999	0.3000	9.131	9.475	9.821	0.6029	0.6191	0.6362	0.7360	0.7313	0.7337
0.4001	0.1999	9.123	9.436	9.807	0.6027	0.6178	0.6358	0.7956	0.7792	0.7754
0.4999	0.0999	9.112	9.417	9.769	0.6023	0.6172	0.6346	0.8460	0.8501	0.8611
0.6000	0.0000	8.972	9.318	9.739	0.5977	0.6139	0.6336	0.9359	0.9351	0.9238
Pentanol + Cyclohexane + n-butyl acetate of system III										
0.0999	0.4999	9.136	9.491	9.849	0.6031	0.6196	0.6371	0.6824	0.6892	0.6976
0.1995	0.4000	9.092	9.482	9.828	0.6016	0.6193	0.6364	0.7045	0.7185	0.7199
0.2998	0.3000	9.070	9.430	9.712	0.6009	0.6176	0.6327	0.7601	0.7707	0.7639
0.4000	0.2000	8.991	9.340	9.676	0.5983	0.6146	0.6315	0.8170	0.8212	0.8213
0.5000	0.1001	8.930	9.174	9.591	0.5962	0.6092	0.6287	0.9103	0.8890	0.8732
0.5992	0.0000	8.707	9.022	9.468	0.5888	0.6041	0.6247	0.9984	0.9879	0.9708
Hexanol + Cyclohexane + n-butyl acetate of system IV										
0.1001	0.5001	9.097	9.505	9.837	0.6018	0.6201	0.6367	0.6847	0.7010	0.7088
0.2000	0.4000	9.012	9.356	9.711	0.5990	0.6152	0.6327	0.7519	0.7615	0.7580
0.2999	0.2999	8.974	9.275	9.498	0.5977	0.6128	0.6257	0.8170	0.8155	0.8095
0.3999	0.1999	8.783	9.160	9.462	0.5913	0.6087	0.6245	0.8747	0.8836	0.8678
0.5000	0.1000	8.653	8.959	9.260	0.5869	0.6020	0.6178	0.9684	0.9561	0.9591
0.6000	0.0000	8.471	8.814	9.019	0.5807	0.5971	0.6097	1.079	1.068	1.059

Volume : 2 | Issue : 9 | September 2013 • ISSN No 2277 - 8179

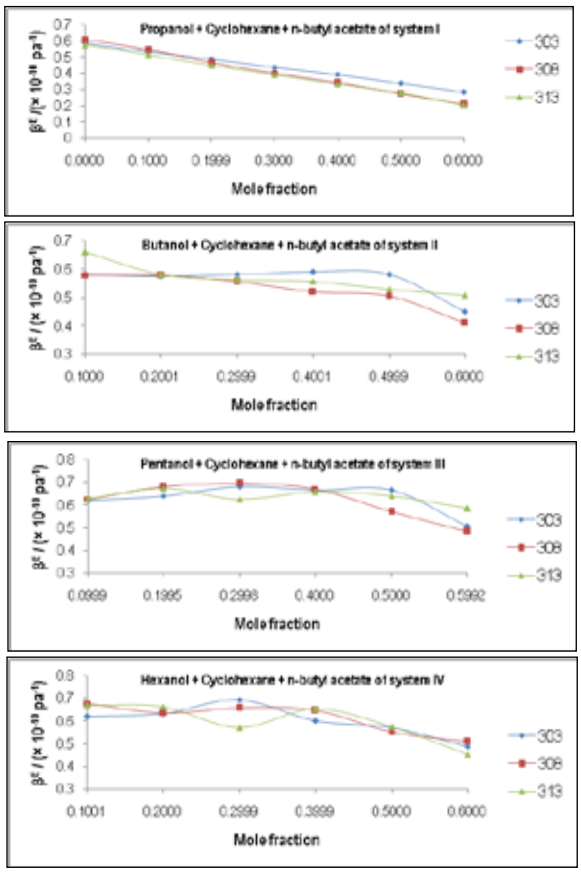

Fig. 1: Excess adiabatic compressibility values vs mole fraction

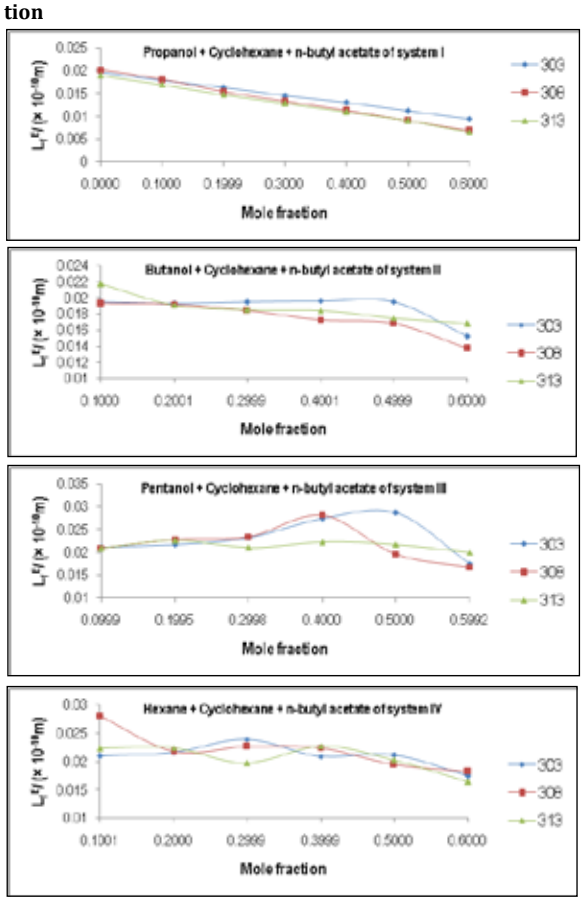

Fig. 2: Excess free length values Vs mole fraction

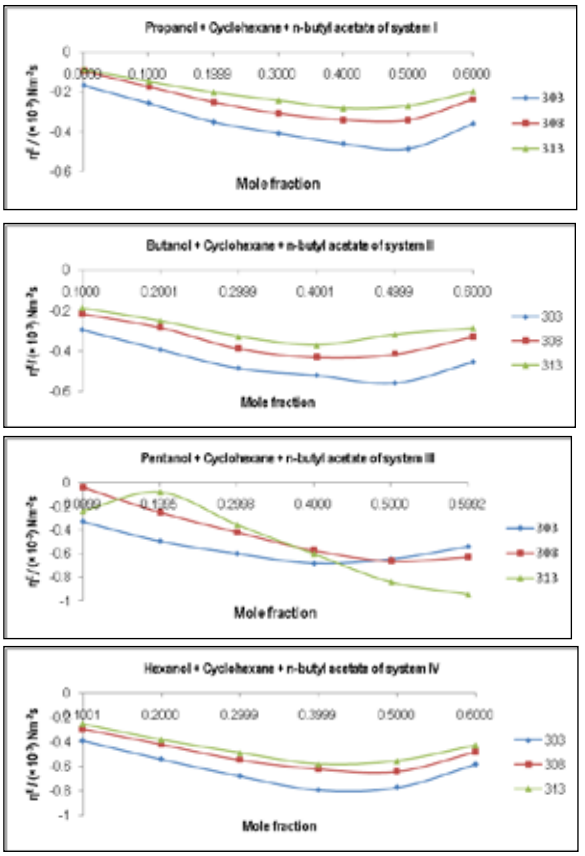

Fig. 3: Excess viscosity values Vs mole fraction

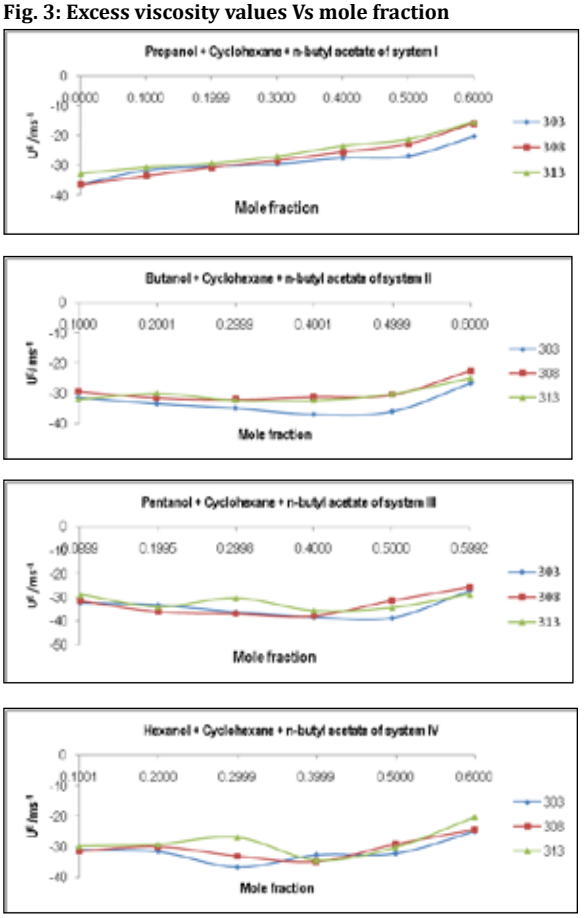

Fig. 4: Excess velocity values Vs mole fraction

REFERENCE

Ali A, Hyder S and Nain A K. 1999. Studies on molecular interactions in binary liquid mixtures by viscosity and ultrasonic velocity measurements at 303.15K. J Mol. Liquids 79: 89-99. | Anil Kumar Nain, 2013. Ultrasonic study of molecular interactions in binary mixtures of methyl acerylate with 1-alkanols (C4 to C10) at temperatures from (288.15 to 318.15K). J. Chem. Thermodynamics, 59: 49-64. | Anwar Ali, M.Kumar and Ibrahim M 2006. volumetric and Ultrasonic Studies of Molecular interactions in binary mixtures of dimethyl sulfoxide with some aromatic hydrocarbons at different temperatures. Bull Chem.Soc Jpn 79: 702-710. | Aravinthraj M. Dineshbabu.N, Kubendran R, Venkatesan.S, and Liakath Ali Khan 2011. Ultrasonic interaction studies between hydrogen bondend ternary mixtures of aniline with aliphatic Ketones in Cyclohexane at different temperatures. Archives of Physics Research 2(1): 254-261. | Asghar.J, Liakath Alikhan.F and Subramani K, 2010. Thermodynamic studies of molecular interactions in Terrary Liquid mixtures at various temperatures. Rasayan J.Chem 3(4): 697-704. | Dash Ashok Kumar and Paikaray Rita 2013. Ultrasonic study on ternary mixture of Diethyl Acetamide (DMAC) in Diethyl either and Acetone, Research Physical Sci. 3: 12-20. | Eyring, H. and Kincaid, J.F. 1938. Free volumes and free angle ratio of molecules in liquids. J. Chem. Phys. 6: 620-629. | Gokhan Savaroglu, Derya Tasagal and Ertunc Aral 2007. Excess molar isentropic compressibilities, excess molar volumes and excess sound speeds of the 1-propanol + diethylether +1-octanol ternary mixture and constituent binary mixtures at 298.15K. Int. J. Thermophysics 28(1). | Gyan Prakash Dubey, Krishnan Kumar and Monika Sharma 2010. Volumetric acoustic and viscometric studies of molecular interactions in binary mixtures of diethylene glycol monomethyl ether with 1-alkanols at temperature from 293.15 to 308.15)K. J. Chem. Thermodynamics 42: 234-243. | Gyan, P. Dubey and Monika Sharma 2008. Study of molecular interactions in binary liquid mixtures of 1-octanol with n-hexane, n-octane and n-decane using volumetric, viscometric and acoustic properties. J. Chem. Thermodynamics, 40: 991-1000. | Iloukhani H and Z. Rostami 2003. Measurement of Some Thermodynamic and Acoustic Properties of Binary Solutions of N,N-Dimethylformamide with 1-Alkanols at 30°C and Comparison with Theories. J Sol. Chem., 32(5): 451-462. | Kumara Sastry. S.V, Shaik. Babu, Ha. SieTiong and Sreehari Sastry.S 2012. Ultrasonic investigation of molecular interactions in Ternary mixtures at 303K. J Chem. Pharm Res 4(4):2122-2125. | Mahendra Nath Roy, Biswajit Sinha and Vikas Kumar Dakua. 2007. Excess molar volumes, viscosity deviations and ultrasonic speeds of sound of binary mixtures of 2-butanone with some alkoxyethanols and amines at 298.15K. J. Mol. Liq. 136: 128-137. | Nikam, P.S., Jagdale, B.S., Sawant, A.B. and Mehdi Hasan, 2000. Sonochemical studies of binary liquid mixtures of toluene with methanol, ethanol, propan-1-ol, butan-1-ol, pentan-1-ol and 2-methylpropan-2-ol at 303.15, 308.15 and 313.15K. Pure. Appl. Ultrason., 22: 115-122. | Praharaj M.K, Satapathy.A, Misra.S and Misra P.R. 2012 Study of Thermodynamic and transport properties of ternary liquid mixtures at different frequencies. J.Chem and Pharm Res 4(4):1910-1920. | Radhamma, M., Venkatesu, P., Prabhakara Rao, M.V., Ming-Jer Lee and Ho-mu Lin. 2008. Excess molar volumes and ultrasonic studies of dimethylsuphoxide with ketones at T = 303.15 K. J. Mol. Thermodyn. 40: 492-497. | Ravichandran.S and Ramanathan.K 2010 Ultrasonic investigations of MnSo4, NiSo4 and CuSo4 Aqueous in Polyvinyl Alcohol Solution At 303K. Rajayan J.Chem 3(2): 375-384. | Ravindranath Reddy, K. and Ramamurthy, L. 1995. Molecular interaction studies in the binary mixtures of aqueous malachite green solution using ultrasonic methods. J. Pure Applied Physics, 17: 45-49. | Satyanaryana Rao, T., Veeriah, N. and Rambabu, C. 2002. Excess volume, viscosity and compressibility of binary mixtures consisting of O-chlorophenol, O-cresol and m-cresol with N,N-dimethlacetamide at different temperatures. Ind. J. Pure Appl. Phys., 40: 850-856. | | Sreekanth K, M. Kondaiah, D. Sravana Kumar, D. Krishna Rao 2012. Excess Acoustical and Volumetric Properties and Theoretical Estimation of Ultrasonic Velocities in Binary Liquid Mixtures of 2-Chloroaniline with Acrylic Esters at 308.15 K. J Solution Chem 41:1088–1102. | Wankhede D.S, Wankhede N.N, Lande M.K, and Arbad B.R.2008. Densities and ultrasonic velocities of some oxygen containing compounds J.Mol.liquids 138:124-129. |