International Journal Of

Recent Scientific Research

ISSN: 0976-3031

Volume: 7(2) February -2016

ULTRASONIC STUDY OF CERTAIN BINARY MIXTURES IN TERMS OF THE EXCESS VALUES OF THERMODYNAMIC PARAMETERS

Manoj Kumar praharaj and Sarmistha Misra

THE OFFICIAL PUBLICATION OF
INTERNATIONAL JOURNAL OF RECENT SCIENTIFIC RESEARCH (IJRSR)
http://www.recentscientific.com/ recentscientific@gmail.com

ISSN: 0976-3031

Available Online at http://www.recentscientific.com

International Journal of Recent Scientific Research
Vol. 7, Issue, 2, pp. 9125-9128, February, 2016

International Journal of Recent Scientific Research

RESEARCH ARTICLE

ULTRASONIC STUDY OF CERTAIN BINARY MIXTURES IN TERMS OF THE EXCESS VALUES OF THERMODYNAMIC PARAMETERS

Manoj Kumar praharaj and Sarmistha Misra

Department of Physics, ABIT, CDA-1, Cuttack, Odisha-753014, India

ARTICLE INFO

Article History:

Received 15th November, 2015
Received in revised form 21st December, 2015
Accepted 06th January, 2016
Published online 28th February, 2016

Keywords:

Benzene, pyridine, toluene, excess values of thermodynamic parameters.

ABSTRACT

The density, viscosity and ultrasonic velocity were measured in binary mixtures of Benzene and cyclohexane, pyridine and cyclohexane, toluene and cyclohexane at different temperatures 288K, 298K, 308K and 318K for a frequency of 6 MHz. The excess values of certain thermodynamic parameters had been calculated from the above experimental data, Analysis of the excess parameters indicates the difference in the molecular interaction existing in the different binary mixtures. It was observed that weak forces like dipole-induced dipole forces and cohesive force sexist between the components of the different binary mixtures.

INTRODUCTION

The ultrasonic velocity in a liquid is fundamentally related to the binding forces between atoms or molecules and has been adequately employed in understanding the nature of molecular interaction in pure liquids and their binary (Praharaj, 2012) and ternary (Thirumaran, 2009) liquid mixtures.

In many industrial applications liquid mixtures rather than single liquid are used in processing and product formulations (Praharaj, 2013). The study of the thermodynamic parameters of the liquid mixtures in terms of their excess values, (Rao, 1981) indicate the departure of their behaviour from ideality which has a great importance in theoretical and applied areas of research.

In the present paper we have studied the excess values of the thermodynamic parameters for three binary mixtures such as

M-I: benzene + cyclohexane,
M-II: pyridine + cyclohexane,
M-III: toluene and cyclohexane.

Benzene (Oswet, 1995) is a non-polar solvent, which is freely miscible with many organic solvents. It has a slightly polar nature due to the delocalised electron cloud which results in the solute solvent molecular associates. Pyridine is a polar aprotic solvent. It is used in a wide variety of reaction including electrophilic substitution, nucleophilicsubstitution, oxidation and reduction as it has the property to form complexes with many salts. Toluene is aprotic and polar in naturedue to the presence of electron releasing methyl group. CH_3 group of toluene is an electron donor group through induction. It enhances the pi-electron density of the toluene ring. Cyclohexane is non-polar un-associated inert hydrocarbon possessing a globular structure. It is highly inert towards electrophile or a nucleophile at ordinary temperature. Due to the non-polar nature of cyclohexane and its inertness towards electron donors, dispersive type of interactions is expected between it and other components.

MATERIALS AND METHODS

The mixtures of various concentrations in mole fraction were prepared by taking analytical reagent grade and spectroscopic reagent grade chemicals with minimum assay of 99.9% and obtained from E-Merck Ltd (India). All the component liquids were purified by the standard methods (Vogal, 1978). The density, viscosity, and ultrasonic velocity were measured as a function of concentration of the binary liquid mixture at

Corresponding author:* **Manoj Kumar praharaj
Department of Physics, ABIT, CDA-1, Cuttack, Odisha-753014, India

temperatures 288K, 298K, 308K and 318K and at frequency 6 MHz.

Ultrasonic velocity measurements were made using an ultrasonic interferometer (Model M-84, supplied by M/S Mittal Enterprises, New Delhi) with the accuracy of ±0.1m·s–1. An electronically operated digital constant temperature bath (Model SSI-03 Spl, supplied by M/S Mittal Enterprises, New Delhi), operating in the temperature range of –10°C to 85°C with an accuracy of ±0.1°C has been used to circulate water through the outer jacket of the double-walled measuring cell containing the experimental liquid. The densities of the mixture were measured using a 10-ml specific gravity bottle by relative measurement method with an accuracy of ±0.01 kg·m^{-3}. An Oswald viscometer (10 ml) with an accuracy of ±0.001 Ns·m^{-2} was used for the viscosity measurement. The flow time was determined using a digital racer stopwatch with an accuracy of ±0.1s.

The following thermodynamic parameters were calculated:

Adiabatic compressibility: $\beta = \frac{1}{\rho.U^2}$ …….**(1)**

Intermolecular free length: $L_f = K_T.\beta^{\frac{1}{2}}$ ……..**(2)**

Where, K_T =(93.875 + 0.375.T) x 10^{-8} is Jacobson's temperature dependent constant .

Free Volume: $V_f = \left(\frac{M_{eff}}{K.\eta}\right)^{\frac{3}{2}}$ ……...**(3)**

Where 'M_{eff}' is the effective mass of the mixture, 'K' is a dimensionless constant independent of temperature and liquid. Its value is 4.281 x 10^9.

Internal Pressure $\pi_i = bRT\left(\frac{K\eta}{U}\right)^{\frac{1}{2}}\left(\frac{\rho^{\frac{2}{3}}}{M_{eff}^{\frac{7}{6}}}\right)$ …….**(4)**

Where, 'b' stands for the cubic packing factor, which is assumed to be '2' for all liquids and solutions. 'K' is a dimensionless constant independent of temperature and nature of liquids. Its value is 4.281x10^9, R is the gas constant, T is the absolute temperature, η is the viscosity, U is the ultrasonic velocity, ρ is the density and M_{eff} is the effective molecular weight.

Acoustic impedance (Z) $Z = \rho.U$ ……. **(5)**

Relaxation time (²) $\tau = \frac{4}{3}.(\beta.\eta)$ ……**(6)**

Gibb's free energy: $\Delta G = KT.ln\left(\frac{KT\tau}{h}\right)$ ……..**(7)**

Where, 'K' is the Boltzmann's constant and '*h*' is the Planck's constant..

Excess Parameters (A^E)

In order to study the non-ideality of the liquid mixtures, the difference between the values of the real mixture (A_{exp}) and those corresponding to an ideal mixture (A_{id}), namely the excess parameters (A^E) were computed using the equation

$A^E = A_{exp} - A_{id}$ ……..**(8)**

Where $A_{id} = \Sigma^n A_i X_i$, '$A_i$,is any parameters and '$X_i$,the mole fraction of the liquid components of 'i'.

RESULTS AND DISCUSSION

Experimental values of density (ρ), viscosity (η) and ultrasonic velocity (U) for the binary systems at temperatures 288 K, 298 K, 308 K and 318 K are presented in table1. Calculated excess values of adiabatic compressibility, free length, internal pressure, viscous relaxation time, Gibbs' free energy and acoustic impedance are tabulated in tables2, 3, 4 and 5. Variations of some parameters with temperature are shown in fig. 1,2 and3.

Table2 Excess values of adiabatic compressibility and free length for binary mixtures at different temperatures

Binarymixture	Excess adiabatic compressibility (β^E) ($10^{-10}N^{-1}.m^2$)				Excess Free length (L_f^E) (10^{-10} m)			
	288K	298K	308K	318K	288K	298K	308K	318K
M-I	0.52	0.350	0.138	0.324	0.020	0.013	0.006	0.012
M-II	0.47	0.461	0.247	0.258	0.022	0.021	0.014	0.014
M-III	0.305	0.251	0.278	0.271	0.012	0.010	0.010	0.010

Table 3 Excess values of free volume and viscous relaxation time for binary mixtures at different temperatures.

Binarym ixture	Excess Free volume (V_f^E) (10^{-7} $m^3.mol^{-1}$)				Excess viscous relaxation time (τ^E) (x 10^{-12} s)			
	288K	298K	308K	318K	288K	298K	308K	318K
M-I	0.298	0.551	0.828	0.894	-0.121	-0.145	-0.149	-0.121
M-II	0.400	0.512	0.546	0.674	-0.272	-0.219	-0.172	-0.153
M-III	-0.70	-1.19	-1.83	-2.60	-0.052	-0.014	0.022	0.048

Excess adiabatic compressibility is positive in all the three cases. This is an indication of structure breaking tendency due to hetero-molecular interaction between the component molecules of the mixture.

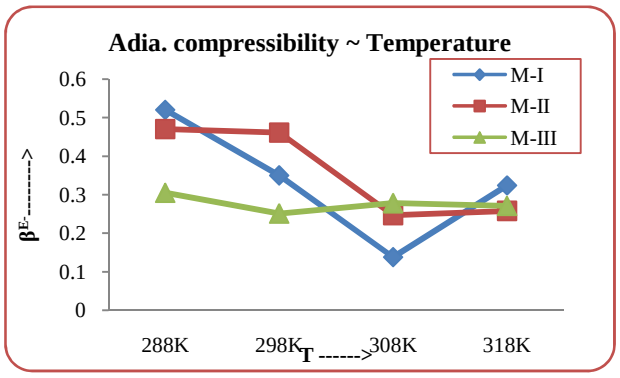
Table 1 Values of density, viscosity and velocity in binary mixtures for different temperatures at 6 MHz frequency.

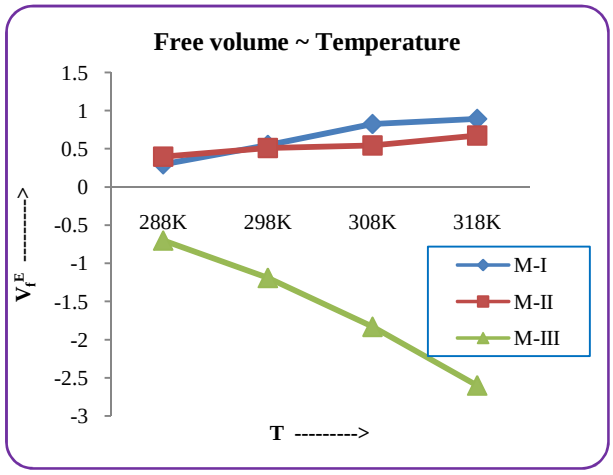
Binarymixture	Density (ρ) Kg.m^{-3}				Viscosity (η) (x10^{-3}N.s.m^{-2})				Velocity (U) m.s^{-2}			
	288K	298K	308K	318K	288K	298K	308K	318K	288K	298K	308K	318K
M-I	835.26	830.94	824.87	818.23	0.912	0.680	0.536	0.459	1280.4	1247.7	1220.1	1165.1
M-II	887.56	882.59	876.93	869.56	1.044	0.829	0.689	0.571	1330.2	1290.5	1265.4	1224.6
M-III	816.85	809.56	802.76	798.41	0.804	0.653	0.538	0.468	1311.2	1269.4	1221.2	1178.4

It also indicates loosely packed molecules, which is as a result of their shape and size.

Table4 Excess values of Gibb's free energy and acoustic impedance forbinary mixtures at different temperatures

Binary mixture	Excess Gibb's free energy (ΔG^E) (x 10^{-20} k.J.mol^{-1})				Excess Acoustic impedance (Z^E)(x 10^6 Kg.m^2.s^{-1})			
	288K	298K	308K	318K	288K	298K	308K	318K
M-I	-0.050	-0.077	-0.097	-0.087	-0.048	-0.031	-0.016	-0.025
M-II	-0.106	-0.105	-0.098	-0.101	-0.084	-0.081	-0.061	-0.059
M-III	-0.012	0.006	0.028	0.051	-0.012	0.006	0.028	0.051





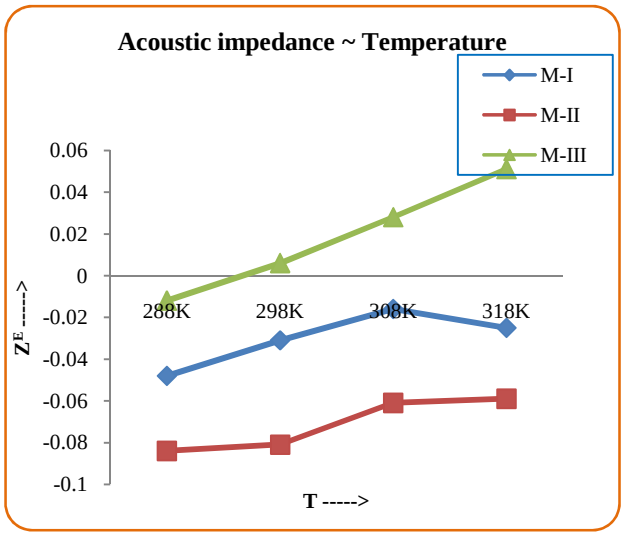


Table 5 Excess values of internal pressure forbinary mixtures at different temperatures.

Binary mixture	Excess internal pressure(Π_i^E) (x 10^6 N.m^{-2})			
	288K	298K	308K	318K
M-I	-41.910	-47.807	-50.595	-46.238
M-II	-100.57	-90.739	-77.068	-73.627
M-III	38.424	44.312	52.384	59.124

Positive value of excess adiabatic compressibility is also confirmed by positive values of excess free length. Forte and Moore indicated that the positive excess values of free length should be attributed to the dispersive forces in general. Excess free length is smallest for the binary mixture toluene+cyclohexane indicating stronger interaction in the same compared to the others. This may be due to the fact that the CH_3 group of toluene enhances the pi-electron of the toluene ring and at the same time increased temperature may break the symmetry of the non-polar cyclohexane molecule creating a donor accepter bond between them.

Excess free volume (Prasad, 2003) is positive in case of benzene+cyclohexane and pyridine+cyclohexane, whereas it is negative for toluene+cyclohexane. The sign of excess free volume depends on the relative strength of the contractive and the expansive forces. The factors responsible for volume contraction are (i) specific interactions between component molecules forming new bonds, (ii) vanderwaal's forces. Factors causing expansion in volume are (i) dispersive forces, (ii) steric hindrance of component molecules (iii) unfavourable geometric fitting and (iv) electrostatic repulsion.

In the first two binary mixtures the positive excess free volume increases as temperature increases indicating increase in intermolecular separation due to dispersive forces. In the binary mixture toluene+cyclohexane the negative value of excess free volume increases with temperature, indicating decrease in free volume. This confirms the fact that a donor accepter bond is created between the two as temperature increases.

Excess internal pressure should be negative when excess free volume is positive and vice versa. This is also confirmed through our observation. Excess relaxation time is negative for benzene+cyclohexane and pyridine+cyclohexane whereas for toluene+cyclohexane it is negative at lower temperature and becomes positive at higher temperature.

Intermolecular interaction in the mixture of benzene+cyclohexane is weak and is of dispersive type. Hence decrease in intermolecular distance is small even at high temperature and thus excess value of relaxation time is negative. However it is less negative compared to that for the mixture pyridine+cyclohexane in which the intermolecular interaction is stronger and is of dipole and induced dipole type. For toluene excess value of relaxation time is negative at low temperature, but almost negligible indicating very weak interaction. At room temperature excess value of relaxation time is negative and large indicating formation of new bonds and hence stronger interaction. As temperature increases excess value of relaxation time becomes positive which is due to large intermolecular distance.

Excess value of Gibbs' free energy is negative for the mixture benzene+cyclohexane and pyridine+cyclohexane while it is negative for toluene+cyclohexane at low temperature and becomes positive as temperature increases. According to Reed etal, the positive value of excess Gibbs' free energy may be attributed to specific interactions which is the case for the binary mixture toluene+cyclohexane at high temperatures. Negative value of excess value of Gibbs' free energy is attributed to the dominance of dispersive forces which is seen in the case of the other two binary mixtures.

Excess acoustic impedance is negative in all the three cases indicating in general weak interaction in all the binary mixtures.

CONCLUSION

From the trends and behaviour of evaluated excess values of the binary mixtures at different temperatures, it is observed that weak forces like dipole-induced dipole forces and cohesive forces exist in them. It also predicts the possibility of a donor acceptor complex in the binary mixture containing toluene and cyclohexane at higher temperatures.

Acknowledgement

We are thankful to the Management of Ajay Binay Institute of Technology, CDA-1, Cuttack, Odisha, for providing the laboratories for the improvement of research activities in the Institute.

Reference

Oswet, S. L., Patel, A. T., 1995.Speeds of sound, isentropic compressibilities, and excess volumes of binary mixtures 2.Mono-n-alkylamines with cyclohexaneand benzene.*J. Chem. Eng. Data*. 40, 194–198.

Paikaray.R., & Mishra.S., 2010.Study of molecular interaction and association in binary mixture of dehpa (Di-(2-ethyl-hexyl) phosphoric acid) with N-butyl chloride at different temperatures.*J. of Acou. Soc. of Ind*. 37(1), 20–24.

Praharaj. M. K., Satapathy. A., Mishra. P. R.,&Mishra.S., 2012.Study of Acoustical and Thermodynamic Properties of Aqueous Solution of NaCl at different Concentrations and Temperatures through Ultrasonic Technique.*Archives of Applied Science Research.* 4 (2): 837-845.

Prasad.N., 2003.Excess free volume and internal pressure of binary solutions of N, N–dimethyl aniline and halomethanes.*J. Pure. App. Ultrason*. 25, 25–30.

Praharaj. M. K., Satapathy. A., Mishra. P. R.,&Mishra.S.,2013.Ultrasonic studies of ternary liquid mixtures of N-N-dimethylformamide, nitrobenzene, and cyclohexane at different frequencies at 318 K,*J. of The.& App. Phy*. 7(23), 1-6.

Rao. D. N., Krishnaiah.A.,& Naidu. P. R.,1981. Excess thermodynamic properties of liquid ethylenediamine + an aromatic hydrocarbon. *Acta. Chim. Acad. Sci. Hung.* 107(1), 49–55.

Thirumaran.S., &Jayakumar.J., 2009.Ultrasonic study of n-alkanols in toluene with nitrobenzene. *Ind. J. Pure & Appl. Phys*. 47, 265–272.

Vogal. A. J., 1978. Practical organic chemistry. 4th edn., Longman, London.

****

How to cite this article:

Manoj Kumar praharaj and Sarmistha Misra.2016, Ultrasonic Study of Certain Binary Mixtures In Terms of The Excess Values of Thermodynamic Parameters. *Int J Recent Sci Res.* 7(2), pp. 9125-9128.

TSSN 0976-3031