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Ultrasonic Study on Biodiesel and Diesel Mixtures

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ABSTRACT

Biodiesel fuel exhibits similar chemical and thermodynamic properties to that of petroleum diesel fuel and hence it is of particular interest to study the molecular association in biodiesel+diesel mixtures. In this regard, the values of sound velocity, density and viscosity were measured at 303 K in the system of biodiesel (sesame oil methyl ester) and diesel. Some of the acoustical parameters such as adiabatic compressibility, free length, free volume and internal pressure were calculated and are interpreted in terms of molecular interaction between the components of the mixtures. The deviations of the sound velocity from that of experimental values were obtained and the collision factor theory was found to be the best suited. The presence of strong interactions was confirmed in the binary system.

Key words: Ultrasonic velocity, density, viscosity, fatty acids, dispersive interaction, excess parameters

INTRODUCTION

The analysis of inter molecular interactions between the components of polar-non-polar liquid mixtures can be conveniently done by ultrasonic methods. Such studies become very significant as they find several applications in industrial and technological processes (Velusamy and Palaniappan, 2011; Rajasekar and Naidu, 1996; Oswal *et al.*, 2004; Arul and Palaniappan, 2001). In modern trend of material characterization the analysis of liquid mixtures by ultrasonic methods has gained much importance in the investigation of the physicochemical behavior and in assessing the type and nature of existing molecular interactions. (Nikam *et al.*, 1999; Alagar *et al.*, 1992). A number of attempts (McClements and Povey, 1987; McClements, 1989; Cebula *et al.*, 1992) have been made to understand the molecular interaction of esters, fats and vegetable oils by employing the ultrasonic velocity measurements.

The use of esterification technology with renewable feed stocks such as waste frying oils, vegetable oils, animal fats etc., leads to the production of biodiesel, which is an alternative diesel fuel (De Oliveira *et al.*, 2005; Powlson *et al.*, 2005). It is an oxygenated, non-toxic, sulphur-free, biodegradable and renewable fuel. The review of literature shows that the biodiesel fuel exhibits similar chemical and thermodynamic properties to that of petroleum diesel fuel (Canakci, 2005; Bijalwan *et al.*, 2006). Hence, it is of particular interest to study the molecular association in biodiesel+diesel mixtures. The present work deals with the measurement of ultrasonic velocity, density, viscosity and computation of related parameters in the binary system of biodiesel and diesel at 303 K.

MATERIALS AND METHODS

Diesel of density 815.6 kg m^{-3} at 303 K is purchased from IOC (Indian Oil Corporation) retail outlet. Biodiesel synthesized by esterification technology is obtained from Department of Bioenergy, School of Energy Sciences, Madurai Kamarajar University, Madurai, Tamil Nadu, India. The biodiesel+diesel mixture of various concentrations in mole fraction were prepared by taking purified samples at 303 K and the mixtures were analyzed for their purity as done by Farooq *et al.* (2008).

The Ultrasonic velocity (U) in liquid mixtures have been measured using an Ultrasonic interferometer (Mittal type) working at 2 MHz frequency with an accuracy of $\pm 0.1 \text{ m sec}^{-1}$. The density (ρ) and viscosity (η) are measured using a pycnometer and an Ostwald's viscometer, respectively, with an accuracy of 3 parts in 10^5 for density and 0.001 Nsm^{-2} for viscosity (Palaniappan, 2001).

Using the measured data, the acoustical parameters such as adiabatic compressibility (β) free length (L_f), free volume (V_f) and internal pressure (π_i) and their excess parameters have been calculated using the following standard expressions (Kannappan and Palaniappan, 1999):

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

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

$$V_f = \left[\frac{M_{\text{eff}} U}{\eta k} \right]^{3/2} \quad (3)$$

$$\pi_i = bRT \left[\frac{k\eta}{U} \right]^{1/2} \left[\frac{\rho^{3/2}}{M_{\text{eff}}^{1/2}} \right] \quad (4)$$

$$A^E = A_{\text{exp}} - A_{\text{id}} \quad (5)$$

and

$$A_{\text{id}} = \sum x_i A_i \quad (6)$$

where, K_T is the temperature-dependent constant (199.53×10^{-8}), k is the temperature independent constant (4.28×10^9) for all liquids, A^E stands for excess property of any given parameter, A_{exp} is the experimental value, A_{id} is the ideal value and $M_{\text{eff}} = \sum x_i m_i$, with x_i as the mole fraction and m_i as the molecular weight of the i th component.

RESULTS AND DISCUSSION

Though biodiesel and diesel have reported to have many similar properties, a sharp change exists in their sound velocity. For pure diesel, sound velocity is $1325.0 \text{ m sec}^{-1}$ but for biodiesel it is $1389.6 \text{ m sec}^{-1}$. The experimental values of density, viscosity and velocity at 303 K for the pure components and for the system diesel+biodiesel are given in Table 1. The perusal of this Table 1 indicates that all the observed parameters in general show an increasing trend with the increasing mole fraction of biodiesel. Biodiesel is denser than diesel and hence the increase in mole fraction of

Table 1: Values of density (ρ), viscosity (η) and ultrasonic velocity (U) at 303 K for biodiesel+diesel mixtures

Mole fraction		ρ (kg m ⁻³)	η ($\times 10^8$ Nsm ⁻²)	U (m sec ⁻¹)
x_1	x_2			
0.0000	1.0000	815.6	4.4888	1325.0
0.0343	0.9657	818.7	4.6270	1327.1
0.0691	0.9309	821.8	4.7685	1329.0
0.1039	0.8961	824.9	4.9137	1331.9
0.1370	0.8630	827.9	5.0615	1334.4
0.1728	0.8272	830.8	5.2128	1336.9
0.2065	0.7935	833.8	5.3672	1339.8
0.2412	0.7588	836.2	5.5243	1342.3
0.2763	0.7237	839.5	5.6850	1345.8
0.3108	0.6892	842.3	5.8483	1347.7
0.3452	0.6548	845.0	6.0142	1350.7
0.3797	0.6203	847.6	6.1827	1353.3
0.4131	0.5869	850.2	6.3532	1356.0
0.4485	0.5515	852.8	6.5268	1358.7
0.4828	0.5172	855.3	6.7022	1361.4
0.5176	0.4824	857.8	6.8796	1363.9
0.5510	0.4490	860.2	7.0580	1366.1
0.5861	0.4139	862.5	7.2394	1368.9
0.6202	0.3798	864.4	7.4212	1371.3
0.6556	0.3444	867.2	7.6051	1373.4
0.6894	0.3106	869.2	7.7898	1375.5
0.7247	0.2753	871.1	7.9748	1377.5
0.7580	0.2420	873.4	8.1609	1379.8
0.7930	0.2070	875.3	8.3460	1381.2
0.8276	0.1724	877.3	8.5331	1382.5
0.8629	0.1371	879.1	8.7190	1384.4
0.8973	0.1027	881.8	8.9063	1385.0
0.9320	0.0680	882.7	9.0917	1387.2
0.9662	0.0338	884.6	9.2768	1388.1
1.0000	0.0000	886.3	9.4610	1389.6

x_1 and x_2 are amount of constituent

the biodiesel seems to increase the mixture density. In the same way, the other observed parameters viz., the sound velocity and the viscosity are also higher for pure biodiesel than pure diesel. The observations found here reflect the existence of interactions between the components as the variations are highly non-linear (Arul and Palaniappan, 2001; Palaniappan, 2001, 2012). The increase in the coefficient of viscosity with increasing mole fraction of biodiesel indicates that the components may either be set away from each other (or) the presence of small size molecules are getting highly restricted.

The calculated values of adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) at 303 K for the pure components and for the mixtures are presented in Table 2. From Table 2, it is found that the adiabatic compressibility shows a reverse trend to that of velocity. The decreasing trends of compressibility with increasing mole fraction of biodiesel reveals that the medium is closely packed which leads to the possibility of the presence of small size components rather than the set away approach as predicted from viscosity variations (Srivastava *et al.*, 2010; Sako *et al.*, 2010). Fatty acids are readily soluble in the organic solvents

Table 2: Values of adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) at 303 K for biodiesel+diesel mixtures

Mole fraction					
x_1	x_2	β ($\times 10^{10}$ Pa $^{-1}$)	L_f ($\times 10^{11}$ m)	V_f ($\times 10^7$ m 3 mol $^{-1}$)	π_i ($\times 10^{-6}$ Pa)
0.0000	1.0000	6.9691	5.2674	0.67551	288.17
0.1000	0.8999	6.8603	5.2261	0.63932	291.05
0.1999	0.8000	6.7238	5.1739	0.54763	303.02
0.3001	0.6999	6.5270	5.0976	0.48704	312.32
0.4002	0.5997	6.3778	5.0389	0.44433	318.66
0.5000	0.4999	6.2966	5.0068	0.41289	322.55
0.6003	0.3997	6.1634	4.9536	0.39129	325.13
0.6998	0.3002	6.0747	4.9178	0.37089	326.49
0.7998	0.2001	6.0069	4.8903	0.35874	329.77
0.8998	0.1002	5.9435	4.8644	0.35381	333.74
1.0000	0.0000	5.8024	4.8063	0.29321	343.81

x_1 and x_2 are amount of constituent

(Gurdeep, 1994; Jacobs, 1951) and diesel is one of the product derived from petroleum, so it may act as solvent in biodiesel+diesel mixture. Hence the addition of solute molecules with reduction in solvent component leads to the separation of polar and non-polar components of solute and ultimately the system exhibits much more compactness (Narendra *et al.*, 2011). Hence the free length decreases in the mixture with increasing biodiesel concentration.

As the unsaturated part is more than the other and as diesel is non-polar, the existence of more number of double bonds in biodiesel component may create an unexpected large interaction between like type as well as in unlike type components (Gopalan, 2002; Rolling and Vogt, 1960). To dissolve the non-polar solute molecule, in general, the solvent should at least have one hydrophobic or like group. This is absent in the present system and hence dispersive type interactions predominates the other. All these processes lead to a decrease in free volume with increase in π_i with increasing mole fraction of biodiesel.

In order to substantiate the presence of interaction between the molecules, it is essential to study the excess parameters. Reddy *et al.* (1964) have commented that the deviation of any physical property from its ideal value is due to the adhesive or cohesive forces between the components and this can be taken as a measure of interaction.

The excess adiabatic compressibility (Fig. 1) and the excess free length (Fig. 2) are mostly negative. The presence of haphazard peaks indicate that the system posses high degree of non-ideality and also the presence of AB interaction. An increase in β^E at 0.2 mole fraction of biodiesel reflects the strong AB interaction leading to complexation. The relative magnitudes of β^E show that the strength of AB interaction decreases as the biodiesel concentration increases.

The role of AB interaction with regards to effective molecular size appears to differ from liquid to liquid (Thirumaran and Thenmozhi, 2010; Rao *et al.*, 2000). The nature of AB interaction existing in the present system is such that it decreases the effective molecular size and thus, leads to negative L_f^E values. The existence of peak values in V_f^E (Fig. 3) again assures the formation of complexation that may be due to the existence of polar saturated components of the fatty acids.

The values of π_i^E (Fig. 4) are randomly fluctuating. Such random variations clearly convey that both dipole-dipole and induced dipole-dipole interactions are existing in the considered system. As

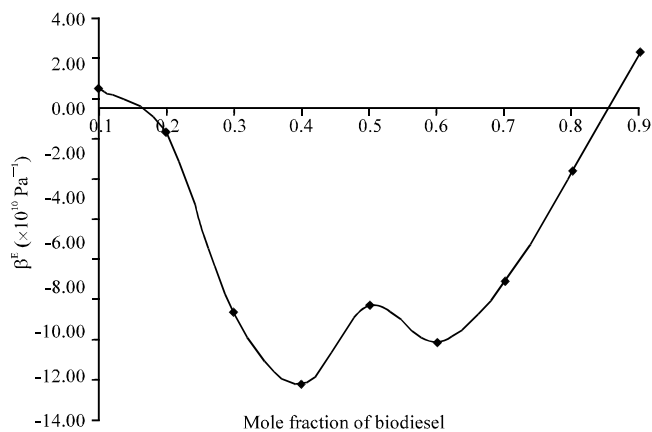


Fig. 1: Mole fraction vs. excess adiabatic compressibility (β^E)

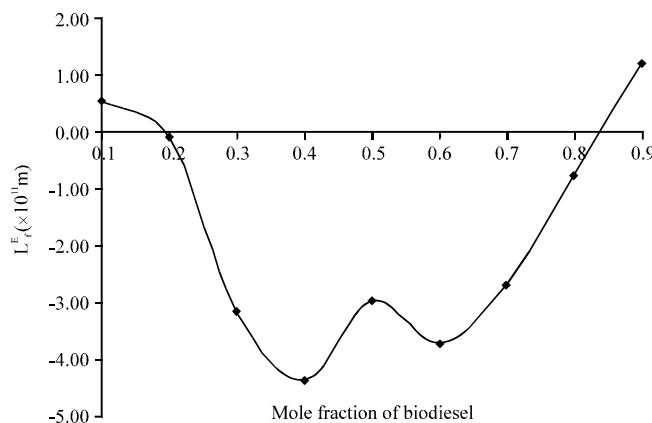


Fig. 2: Mole fraction vs. excess free length (L_f^E)

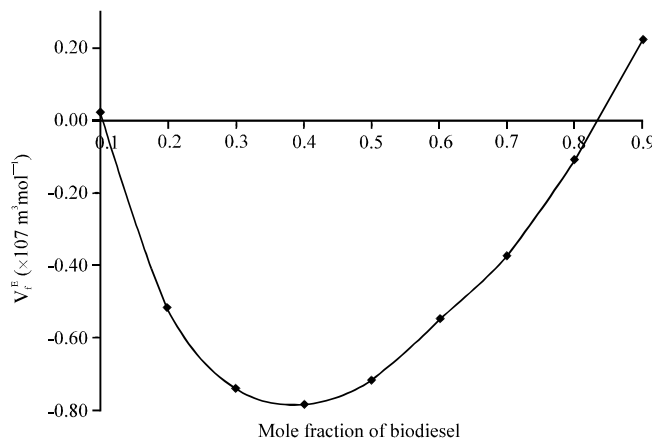


Fig. 3: Mole fraction vs. excess free volume (V_f^E)

there are huge fluctuations in these parameters, the chances of induced dipole-dipole interaction are more and the strong dipolar type interactions are additionally confirmed.

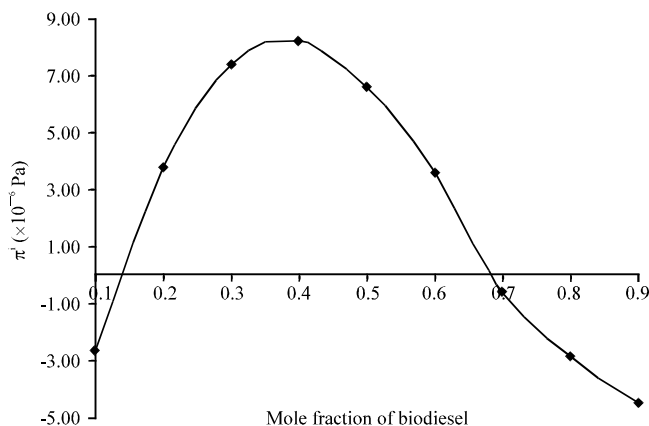


Fig. 4: Mole fraction vs. excess internal pressure (π^i)

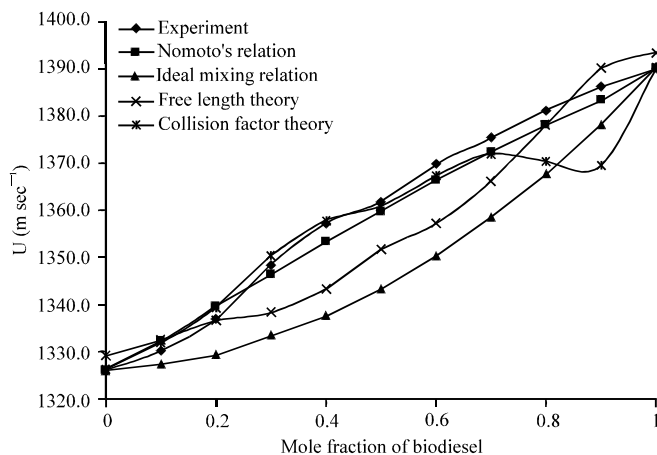


Fig. 5: Mole fraction vs. ultrasonic velocity (U)

Deviation of the experimentally extracted velocity from the theoretical values could indicate to the great extent the role of biodiesel and in this aspect, three theoretical models such as Free Length Theory (FLT), Nomoto's Relation (NR) and Ideal Mixture Relation (IMR) have been considered. The trends of sound velocity estimated by the various methods along with the experimental are shown in Fig. 5, which clearly reveals that the NR shows a unanimous agreement with that of the experimental values. However, at higher and lower mole fraction of biodiesel, FLT offers a correlation as best as that of CFT with the experimental values whereas in intermediate mole fractions, both CFT and NR offers an equal correlation.

As intermolecular interactions are expected to be much more at equimolar concentrations, the order of merit for the prediction of sound velocity goes down as CFT, NR and FLT. The prediction obtained from the molecular interaction parameter clearly supports the previous conclusion that more number of small size components exists and this leads to close packing nature even though dispersive type interactions are predominating. The least agreement of FLT further confirms that the system is not associative one.

CONCLUSION

Presence of small size molecules is found to be highly restricted. Strong intermolecular interactions are noticed in the system and the components of the system show a high degree of dissociation.

REFERENCES

- Alagar, M., M. Ponnusamy and A. Amsavel, 1992. Ultrasonic properties of some silicate esters. *Hungar J. Ind. Chem.*, 20: 1-4.
- Arul, G. and L. Palaniappan, 2001. Molecular interaction studies in the ternary mixtures of cyclohexane + toluene + 2-propanol. *Indian J. Pure Applied Phys.*, 39: 561-564.
- Bijalwan, A., C.M. Sharma and V.K. Kediya, 2006. Bio-diesel revolution. *Sci. Rep.*, 43: 14-17.
- Canakci, M., 2005. Performance and emissions characteristics of biodiesel from soybean oil. *J. Automobile Eng.*, 219: 915-922.
- Cebula, D.J., D.J. McClements, M.J.W. Povey and P. Smith, 1992. Neutron diffraction studies of liquid and crystalline trilaurin. *J. Am. Oil. Chem. Soc.*, 69: 130-136.
- De Oliveira, D., M. Di Luccio, C. Faccio, C.D. Rosa and J.P. Bender *et al.*, 2005. Optimization of alkaline transesterification of soybean oil and castor oil for biodiesel production. *Appl. Biochem. Biotechnol.*, 121-124: 553-560.
- Farooq, R., S.F. Shaikat, A.K. Khan and U. Farooq, 2008. Ultrasonic induced decomposition of methidathion pesticide. *J. Applied Sci.*, 8: 140-145.
- Gopalan, C., 2002. Nutritive value of Indian foods. National Institute of Nutrition, Indian Council of Medical Research, Hyderabad, pp: 86.
- Gurdeep, R.C., 1994. Organic Chemistry of Natural Products. Himalaya Publishing House, Nagpur, India, ISBN: 9788170409991, pp: 642-643.
- Jacobs, M.B., 1951. The Chemistry and Technology of Food and Food Products. 2nd Edn., Vol. 1, Interscience Publishers, New York, pp: 107.
- Kannappan, A.N. and L. Palaniappan, 1999. Molecular association studies of 1-propanol in cyclohexane with benzene. *Indian. J. Phys.*, 73: 531-536.
- McClements, D.J. and M.J.W. Povey, 1987. Solid fat content determination using ultrasonic velocity measurements. *Int. J. Food Sci. Technol.*, 22: 491-499.
- McClements, D.J., 1989. The use of ultrasonics for characterizing fats and emulsions. Ph.D. Thesis, Department of Food Science, University of Leeds.
- Narendra, K., P. Narayanamurthy and C. Srinivasu, 2011. Refractive indices of binary liquid mixture at different temperatures. *Asian J. Applied Sci.*, 4: 535-541.
- Nikam, P.S., T.R. Mahale and M. Hassan, 1999. Molecular interactions in binary mixtures of ethyl acetate with 1-pentanol, 1-hexanol, 3,5.15K: An ultrasonic study, *Indian. J. Pure Appl. Phys.*, 37: 92-96.
- Oswal, S.L., N.Y. Ghael and K.D. Prajapati, 2004. Speeds of sound, isentropic compressibilities, viscosities and excess molar volumes of cyclohexanol+cyclohexane at 303.15 K. *Thermochim. Acta*, 419: 59-65.
- Palaniappan, L., 2001. Ultrasonic study of 2-butanol in cyclohexane with toluene. *Indian J. Phys.*, 75: 515-518.
- Palaniappan, L., 2012. Ultrasonic analysis of intermolecular interaction in the mixtures of benzene with methanol, ethanol, 1-propanol. *Asian J. Mater. Sci.*, 4: 21-27.

- Powlson, D.S., A.B. Riche and I. Shield, 2005. Biofuels and other approaches for decreasing fossil fuel emissions from agriculture. *Ann. Applied Biol.*, 146: 193-201.
- Rajasekar, J. and P.R. Naidu, 1996. Speed of sound of 1,3-dichlorobenzene + methyl ethyl ketone + 1-alkanols at 303.15 K. *J. Chem. Eng. Data*, 41: 373-375.
- Rao, S., B.V. Naidu and C. Rao, 2000. Ultrasonic study of some binary liquid mixtures. *J. Acoust. Soc. India*, 28: 303-308.
- Reddy, K.C., S.V. Subrahmanyam and J. Bhimasenachar, 1964. Thermodynamics of binary liquid mixtures containing cyclohexane part 1. *J. Phys. Soc. Japan*, 19: 559-559.
- Rolling, R.E. and C.J. Vogt, 1960. The adiabatic bulk modulus of normal paraffin hydrocarbons from hexane to hexadecane. *J. Basic Eng.*, 82: 635-644.
- Sako, A., A. Memeledje and P. Assamoi, 2010. Measurement of the viscosity of mousse myoblasts modified with the α β crystalline through the technique of micromanipulation by the means of micropipette. *Asian J. Applied Sciences*, 3: 250-261.
- Srivastava, R., A.R. Saksena and A. Gupta, 2010. Viscometric studies on the molecular association of biomolecules based on thermodynamic parameters supported by UV spectra. *Asian J. Applied Sci.*, 3: 13-24.
- Thirumaran, S. and P. Thenmozhi, 2010. Study of molecular interaction in ternary liquid mixtures by ultrasonic velocity measurements. *Asian J. Applied Sci.*, 3: 153-159.
- Velusamy, V. and L. Palaniappan, 2011. Compositional analysis α -lactalbumin. *Am. J. Biochem. Mol. Biol.*, 1: 106-120.