RJC

RASĀYAN *J. Chem.*
Vol. 11 | No. 3 |984 - 989 | July - September | 2018
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

DENSITY AND ACOUSTIC PROPERTIES OF BINARY LIQUID MIXTURES OF ETHYL ACETOACETATE (EAA) WITH 1-ALKANOLS (C_3-C_6) AT TEMPERATURE 303.15K

T. Savitha Jyostna*, G. Ramesh, D. Sreenu and B. Satheesh
Department of Chemistry, Kakatiya University, Warangal-506009(T.S), INDIA
*E-mail:savithajyostna@gmail.com

ABSTRACT

The density and speed of sound of binary liquid mixtures of Ethyl acetoacetate with 1-Propanol, 1-Butanol, 1-Pentanol and 1-Hexanol have been measured over the entire range of composition at 303.15K temperature. From these data, excess thermodynamic parameters namely excess molar volume and deviation in isentropic compressibility have been calculated. The calculated parameters have been fitted to Redlich-Kister type polynomial equation. The values of excess parameters have been explained in terms of molecular interactions that operating between unlike molecules in the binary liquid mixtures of Ethyl acetoacetate with 1-Alkanols.

Keywords: density, the speed of sound, excess molar volume, isentropic compressibility, Redlich-Kister polynomial equation, molecular interactions.

INTRODUCTION

The thermodynamic properties of binary liquid mixtures is an important role in many industrial applications such as density, viscosity, the speed of sound, refractive index, etc are often used for the determination of excess thermodynamic properties of binary liquid mixtures[1-4]. In view of that the calculated excess thermodynamic parameters i.e., excess molar volume (V^E)and deviation in isentropic compressibility($\Delta\kappa s$) are essential in most of the engineering calculations, many practical problems concerning mass transferapplications[5].Generally, on mixing of two liquids into a liquid mixture may result in deviation from ideal behavior, in this concern most of the research workers showing interest to determine the nature of molecular interactions between unlike molecules in the binary liquid mixture[6,7].

The present work analyzes the excess parameters of binary liquid mixtures of Ethyl acetoacetate (EAA) with 1-Propanol, 1-Butanol, 1-Pentanol and 1-Hexanol (1-Alkanol). These EAA and 1-Alkanols are polar organic liquids, EAA mainly used as a chemical intermediate in the production of a wide variety of compounds[8,9], and 1-Akanol molecules are self-associated through hydrogen bonding of their hydroxyl groups and widely used as a solvent in many organic reactions[10].

The experimental data of density (ρ) and speed of sound (u) for the binary liquid mixtures of EAA with 1-Alkanols at 303.15 K temperature and atmospheric pressure has been reported in present work. Moreover, the excess molar volume (V^E), and deviation in isentropic compressibility ($\Delta\kappa_S$) have been calculated and fitted to Redlich-Kister polynomial type equation, these parameters used to study the interactions between unlike molecules of investigated binary liquid mixtures.

EXPERIMENTAL

Materials

EAA, 1-Propanol, 1-Butanol, 1-Pentanol, and 1-Hexanol used for the entire mole fraction was purchased from Alfa-Aesar with ≥ 99% purity. They were used without further purification. The purities of the materials were checked by comparing their density (ρ) and speed of sound (u) values were determined at a 303.15K temperature and compared with literature data[11-16]and reported in Table-1.

http://dx.doi.org/10.31788/RJC.2018.1132041

CrossMark

Apparatus and Procedure

The mixtures were prepared by weighing an appropriate volume of the sample mixtures in air tight stopper bottles to minimize the evaporation and contamination of solvents. Weight measurements of binary mixtures were made on Dhona (100DS), India, having single-pan analytical balance, with a precision of $\pm 1 \times 10^{-8}$ kg. The probable error in mole fraction was estimated to be less than $\pm 1 \times 10^{-4}$.The density and related molar volume properties of the mixtures were measured on the same day, the uncertainty in density was found to be 5×10^{-2} kg.m^{-3}. Later on, mixing the sample thoroughly with bubble free and it was transferred into a U-shaped double-arm pycnometer using syringe[17]. The pycnometer was calibrated using double distilled water having a conductivity less than 1×10^{-6} Ω^{-1} cm^{-1} (density is 0.9970 g.cm^{-3}) at different temperatures[2].

The speed of sound measurements was determined for liquid mixtures by using an ultrasonic interferometer [model M-82, Mittal Enterprise, India] working at a frequency of 2 MHz with a measuring cell[18]. The relative uncertainty measurements of the speed of sound were found to be ±0.3%. During the measurements of density (ρ) and speed of sound (u) the temperature was controlled within $\pm 1 \times 10^{-2}$ K by using a constant temperature bath [INSREF model; IRI-016 C, India].

Table-1: Comparison of Experimental Values of Density (ρ) and Speed of Sound (u) with Literature Values of Components at T=303.15K.

Liquid	ρ (10^{-3}.kg m^{-3})		u (m s^{-1})	
	Expt	Lit	Expt	Lit
EAA	1.0148	1.0149 [11]	1312.6	1331.0* [11]
1-Propanol	0.7967	0.7964 [12]	1190.0	1189.0 [15]
1-Butanol	0.8020	0.8020 [13]	1224.1	1222.0 [15]
1-Pentanol	0.8068	0.8071 [14]	1259.0	1258.0 [16]
1-Hexanol	0.8115	0.8116 [14]	1288.0	1288.0 [16]

*at 298.15K

RESULTS AND DISCUSSION

The experimental data of density (ρ) and speed of sound (u) of binary liquid mixtures of EAA with 1-Alkanols at 303.15K along with calculated mole fraction values have given in Table-2.

The excess molar volumes (V^E) have been calculated from density using the following equations:

$$V^E = (x_1M_1+x_2M_2)/\rho_m-(x_1M_1/\rho_1+x_2M_2/\rho_2) \quad (1)$$

Where ρ_m is the density of the liquid mixture, x_1 and x_2 are mole fractions, M_1 and M_2 are molar masses, ρ_1 and ρ_2 are densities of pure components 1 and 2, respectively.

The speed of sound (u) was used to calculate the isentropic compressibility (κ_s) using the equation:

$$\kappa_s = u^{-2}.\rho^{-1} \quad (2)$$

The excess isentropic compressibility ($\Delta\kappa_s$) has been evaluated using the equation:

$$\Delta\kappa_s = \kappa_s-(\Phi_1\kappa_{s1}+\Phi_2\kappa_{s2}) \quad (3)$$

Where κ_{s1}, κ_{s2} and κ_s are the isentropic compressibility of the pure components and observed isentropic compressibility of liquid mixture respectively.$\Phi_1$and $\Phi_2$are the volume fraction of pure components 1 and 2, respectively. The values of Φ_i is computed from the individual molar volumes V_i, using the relation,

$$\Phi_i = x_iV_i/(\Sigma x_iV_i) \quad (4)$$

The excess molar volumes (V^E), deviation in isentropic compressibility ($\Delta\kappa_s$) for the binary mixtures were fitted to a Redlich–Kister polynomial type of equation by the method of nonlinear least-squares[19].

$$\Delta Y = x_1 x_2\Sigma a_i (x_1-x_2)^i \quad (5)$$

Where a_0, a_1, a_2, a_3 and a_4 are adjustable binary coefficients. The coefficients a_i is estimated using multi parametric regression analysis based on a non-linear least-squares method. The number of a_i parameters

are optimized using the F-test and is found to be five (m=5). In each case, the optimum number of coefficients a_i is determined from an examination of the variation of standard deviation (σ) as calculated by:

$$\sigma (Y^E) = [\Sigma (\Delta Y_{obs} - \Delta Y_{cal})^2 / (n-m)]^{1/2} \quad (6)$$

Where n, m, are a number of experimental points and number of coefficients used in fitting the data. The coefficients a_i and standard deviations (σ) of V^E, and $\Delta\kappa_s$ are summarized in Table-3.

The excess molar volume (V^E) for binary mixtures of EAA (1) + 1-alkanols (2) is presented at 303.15K in Table-2. The excess molar volume (V^E) data with a mole fraction of EAA is graphically represented at 303.15K in Fig.-1, which indicates that, positive values of V^E over the whole mole fraction range. The positive V^E values can be attributed to some factors i.e., breaking of H-bonds in 1-alkanols in the presence of EAA, dispersion forces and weak dipole–dipole interactions are operating between unlike molecules. Moreover, dispersion forces increase with an increase in the chain length of alcohols[20].

The algebraic values of V^E for the mixtures of EAA with 1-alkanols at equimolar composition of all binary systems are as follows in the order:

(EAA+1-Hexanol) **>** (EAA+1-Pentanol) **>** (EAA+1-Butanol) **>** (EAA+1-Propanol) **>** 0

The deviation in isentropic compressibility ($\Delta\kappa_s$) for mixtures of EAA (1) +1-alkanols (2) is presented at 303.15K in Table-2. The deviation in isentropic compressibility ($\Delta\kappa_s$) data with a mole fraction of EAA is graphically represented at 303.15K in Fig.-2, which indicates that, negative values of $\Delta\kappa_s$ over the whole mole fraction range. The $\Delta\kappa_s$ values attributed to the changes in intermolecular free space, these changes arise due to structure-breaking and structure-making effects of the components and the subsequent change in geometrical factors[21]. Structure-breaking effect contributes to increases in free space between the molecules, this leads to the positive $\Delta\kappa_s$. On the other hand, structure-making effects would contribute to decreasing in free space[22] and a negative $\Delta\kappa_s$. The investigated results indicate that the structure-making effect is developed due to the dipole-dipole interactions exist between unlike molecules and dominated in all binary mixtures of EAA with 1-alkanols. The algebraic values of $\Delta\kappa_s$ for the mixtures of EAA with 1-alkanols at the equimolar composition of all binary systems are as follows in the order:

0 **>** (EAA+1-Hexanol) **>** (EAA+1-Pentanol) **>** (EAA+1-Butanol) **>** (EAA+1-Propanol)

Table-2: Values of Density (ρ), Excess Molar Volume (V^E), the Speed of Sound (u) and Deviation in Isentropic Compressibility ($\Delta\kappa_s$) for the Binary Liquid Mixtures at T=303.15K

X_1	$\rho.10^{-3}$ (Kg m^{-3})	$V^E.10^6$(m^3 mol^{-1})	u (m s^{-1})	$\Delta\kappa_s.10^{11}$(m^2 N^{-1})
EAA (1)+1-Propanol(2)				
0.0000	0.7967	0.0000	1190.0	0.0000
0.0644	0.8195	0.0092	1206.8	-2.8185
0.1297	0.8406	0.0204	1220.1	-4.6423
0.2035	0.8624	0.0326	1232.7	-5.9296
0.2808	0.8833	0.0435	1245.0	-6.7662
0.3716	0.9055	0.0540	1257.3	-7.0920
0.4706	0.9274	0.0638	1268.6	-6.8348
0.5808	0.9492	0.0716	1281.2	-6.1902
0.7083	0.9716	0.0733	1294.4	-4.9390
0.8379	0.9921	0.0496	1304.7	-3.0777
1.0000	1.0148	0.0000	1312.6	0.0000
EAA(1)+1-Butanol(2)				
0.0000	0.8020	0.0000	1224.1	0.0000
0.0770	0.8228	0.1500	1235.6	-1.6010
0.1552	0.8431	0.2404	1246.0	-2.7817
0.2375	0.8636	0.3021	1254.8	-3.4939
0.3240	0.8840	0.3471	1264.1	-3.9948

0.4191	0.9052	0.3806	1273.7	-4.2163
0.5209	0.9266	0.4004	1282.5	-4.0488
0.6261	0.9476	0.3754	1291.0	-3.6107
0.7400	0.9692	0.3165	1298.6	-2.7774
0.8610	0.9909	0.2089	1305.3	-1.5831
1.0000	1.0148	0.0000	1312.6	0.0000
EAA(1)+1-Pentanol(2)				
0.0000	0.8068	0.0000	1259.0	0.0000
0.0902	0.8258	0.3592	1267.4	-0.9146
0.1791	0.8453	0.5299	1274.0	-1.5407
0.2695	0.8649	0.6362	1279.5	-1.9062
0.3621	0.8846	0.7091	1285.1	-2.1371
0.4424	0.9014	0.7431	1289.5	-2.1867
0.5633	0.9263	0.7409	1296.0	-2.0937
0.6447	0.9430	0.6900	1300.2	-1.9254
0.7739	0.9691	0.5463	1306.8	-1.5163
0.8864	0.9915	0.3537	1310.6	-0.8650
1.0000	1.0148	0.0000	1312.6	0.0000
EAA(1)+1-Hexanol(2)				
0.0000	0.8116	0.0000	1288.0	0.0000
0.1053	0.8294	0.5951	1291.3	-0.4277
0.1983	0.8472	0.7894	1294.0	-0.7195
0.2962	0.8667	0.8489	1296.1	-0.9905
0.3947	0.8867	0.8585	1298.8	-1.2322
0.4947	0.9073	0.8081	1298.3	-1.3284
0.5989	0.9289	0.7201	1303.6	-1.3069
0.6989	0.9498	0.6151	1302.2	-1.1735
0.7954	0.9702	0.4703	1307.5	-0.7681
0.8920	0.9909	0.2945	1310.2	-0.3478
1.0000	1.0148	0.0000	1312.6	0.0000

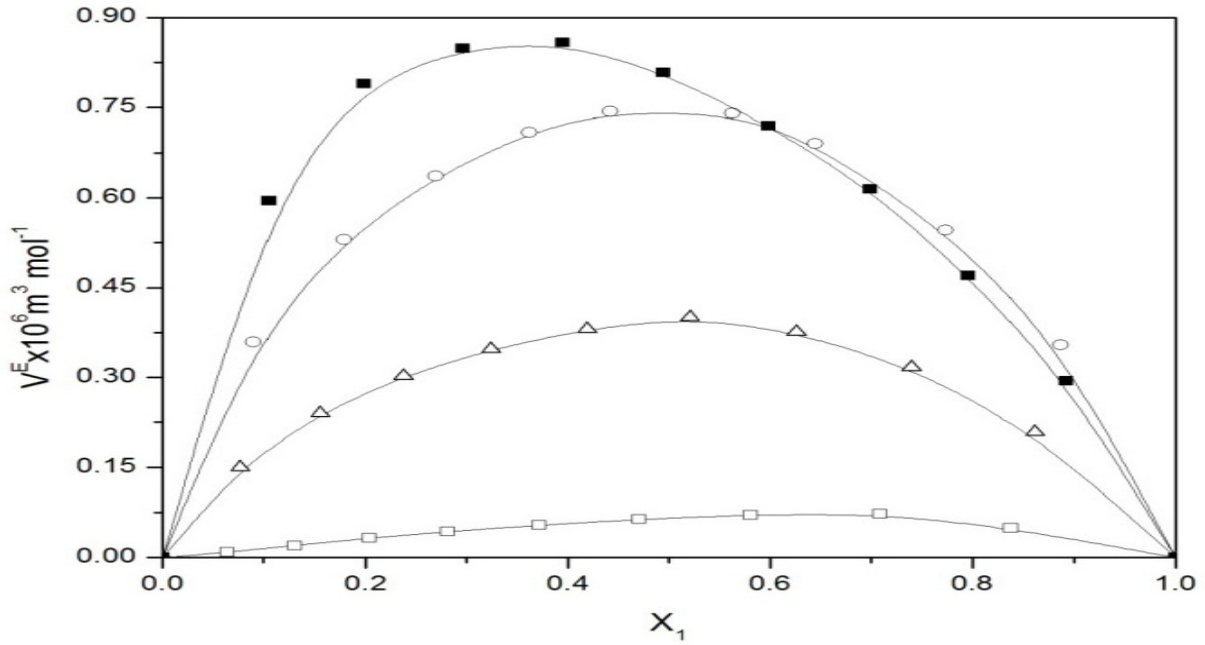

Fig.-1: Plot of V^E against mole fraction of EAA (1) with □; 1-Propanol (2), Δ; 1-Butanol (2) O; 1-Pentanol (2), ■; 1-Hexanol (2) at T= 303.15K

Table-3: Adjustable parameters (*A*i) and standard deviations (σ) for the binary mixtures of EAA (1) +1-Alkanols (2) at T=303.15K.

System	Property	A_0	A_1	A_2	A_3	A_4	σ
EAA+1-Propanol	$V^E.10^6(m^3\ mol^{-1})$	0.266	0.184	0.144	-0.121	-0.250	0.001
	$\Delta\kappa_s.10^{11}(m^2\ N^{-1})$	-27.070	10.144	-5.737	4.439	-5.995	0.049
EAA+1-Butanol	$V^E.10^6(m^3\ mol^{-1})$	1.583	0.089	0.115	-0.345	0.613	0.002
	$\Delta\kappa_s.10^{11}(m^2\ N^{-1})$	-16.435	4.359	-1.740	2.356	0.349	0.026
EAA+1-Pentanol	$V^E.10^6(m^3\ mol^{-1})$	3.011	-0.056	0.215	-0.571	1.904	0.001
	$\Delta\kappa_s.10^{11}(m^2\ N^{-1})$	-8.638	1.224	-2.753	0.500	1.380	0.015
EAA+1-Hexanol	$V^E.10^6(m^3\ mol^{-1})$	3.224	-1.241	1.363	-1.307	1.592	0.004
	$\Delta\kappa_s.10^{11}(m^2\ N^{-1})$	-5.385	-1.274	1.770	3.041	0.626	0.022

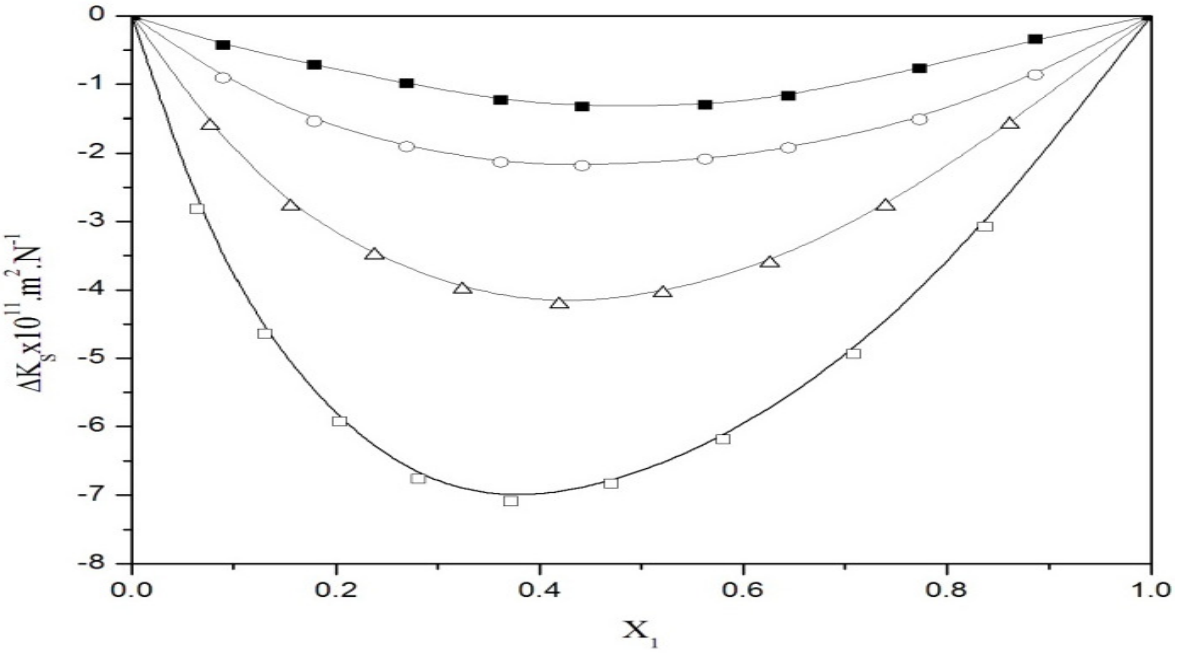

Fig.-2: Plot of $\Delta\kappa_s$ against mole fraction of EAA (1) with □; 1-Propanol (2), Δ; 1-Butanol (2), O; 1-Pentanol (2), ■; 1-Hexanol (2) at T= 303.15K

CONCLUSION

Densities and speed of sound for binary mixtures of EAA with 1-Alkanols have been measured at 303.15 K. From the data the V^E and $\Delta\kappa_s$ have been calculated. The excess molar volume (V^E) is positive, and deviation in isentropic compressibility ($\Delta\kappa_s$) is negative for all the mixtures at all composition considered in this work. The experimental results indicate that weak dipole–dipole interactions are operating between unlike molecules and dominated in all liquid mixtures. The results are correlated using the Redlich–Kister type polynomial equation and binary coefficients along with standard deviations are also reported.

ACKNOWLEDGMENT

The authors are grateful to University Grants Commission (UGC-JRF), Government of India, for the financial support.

REFERENCES

1. T. S. Jyostna, N. Satyanarayana, *J. Chem. Thermodyn.*, **38**, 272(2006), **DOI:** 10.1016/j.jct.2005.05.006
2. B. Sathyanarayna, K. B. Ranjith, T. S. Jyostna, N. Satyanarayana, *J. Chem. Thermodyn.*, **39,** 16(2007), **DOI:** 10.1016/j.jct.2006.06.009

3. Sk. S. Shihab, K. G. Rao, M. G. Kiran, Sk. Babu, S. S. Sastry, *Rasayan J. Chem.*,**10(1)**, 59(2017) **DOI:** 10.7324/RJC.2017.1011552
4. N. Raghuram, R. Suresh, G. Ramesh, G. Sowjanya, T. S. Jyostna, *J .Therm. Anal. Calorim.,* **119,** 2107(2015), **DOI:** 10.1007/s10973-015-4399-1
5. P. Venkatesu, M. V. Rao, *J. Chem. Eng. Data.*, **42**, 90(1997), **DOI:** 10.1021/je960228v
6. L. Venkatramana, R. L. Gardas, K. Sivakumar, K. D. Reddy, *Fluid Phase Equilib.*, **367**, 7(2014) **DOI:** 10.1016/j.fluid.2014.01.019
7. P. S. Nikam, L. N. Shrisat, M. B. Hasan, *J. Chem. Eng. Data.*, **43**,732(1998), **DOI:** S0021-9568(98)00028-4
8. Y. W. Sheu, C. H. Tu, *J. Chem. Eng. Data.,* **51**, 545(2006), **DOI:** 10.1021/je050402s
9. N. Indraswati, Mudjijati, F. Wicaksana, H. Hindarso, S. Ismadji, *J. Chem. Eng. Data.,***46**, 696(2001), **DOI:** 10.1021/je000382o
10. C. D. Eads, *J. Phys. Chem. B*,**104**, 6653(2000), **DOI:** 10.1021/jp993472c
11. J. N. Nayak, M. I. Aralaguppi, T. M.Aminabhavi, *J. Chem. Eng. Data.,* **48**,1489(2003), **DOI:** 10.1021/je0301489
12. F. M. Pang, C. E. Seng, T. T. Teng, M. H. Ibrahim, *J. Mol. Liquids.*, **136**,71(2007) **DOI:** 10.1016/j.molliq.2007.01.003
13. E. Z. Bski, A. Waligora, *J. Chem. Eng. Data.,* **53,** 591(2008), **DOI:** 10.1021/je700580g
14. H.E. Hoga, R. B. Torres, *J.Chem.Thermodyn.,***43**,1104(2011), **DOI:** 10.1016/j.jct.2011.02.018
15. S. Sangeeta, A. Martin, D. Nirmala, *J. Chem. Thermodyn.*, **57**, 238(2013) **DOI:**10.1016/j.jct.2012.08.030
16. M. S. AlTuwaim, A. Haek, S. A. A. Jimaz, A. A. Mohammad, *J. Chem. Thermodyn.*,**48**, 39 (2012), **DOI:** 10.1016/j.jct.2011.12.002
17. K. Sreenivasulu, R. L. Gardas, P. Venkatashwarlu, K. Sivakumar, *J. Chem.Thermodyn.,* **67**, 203(2013), **DOI:** 10.1016/j.jct.2013.08.013
18. N. Satyanarayana, B. Sathyanarayna, T. S. Jyostna, *J. Chem. Eng. Data.*, **52,**405(2007), **DOI:** 10.1021/je060343y
19. O. Redlich, A. Kister, *Ind. Eng. Chem.*, **40**, 345(1948), **DOI:** 10.1021/ie50458a036
20. B. Garcio, S. Aparicio, A. M. Navarro, R. Alcalde, J. M Leal, *J. Phys. Chem.B.*, **108**,15841(2004) **DOI:** 10.1021/jp0485439
21. B. Jacobson, *J. Chem. Phys.*, **20**, 927(1952), **DOI:**10.1063/1.1700615
22. S. S. Sastry, B. Shaik, T. Vishwam, S. T. Ha, *Physics and Chemistry of Liquids.*, **52**, 272(2014) **DOI:**10.1080/00319104.2013.820302

[RJC-2041/2018]