



Physicochemical study of a binary liquid mixture by ultrasonic speed, isentropic compressibility and acoustic impedance from 288.15-318.15K

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Abstract

Ultrasonic study of intermolecular interactions between the solvents of different nature have been performed by ultrasonic speed (U), isentropic compressibility (β_s) and acoustic impedance (Z). Ultrasonic speed and aforesaid acoustical parameters for binary liquid mixture of 2-butanol and dodecane were computed from 288.15-318.15K over the entire range of concentration and atmospheric pressure and compared with the literature values Paterson-Flory-Prigogine (PFP), Ramaswamy- Anbananthan (RS) and Glinski model (GLI) were used to study the intermolecular interactions between the poor interacting liquids at different temperatures. Standard deviations and numerical coefficients of mixing properties were estimated by Redlich Kister polynomial. McAllister multibody correlation model was used to correlate the experimental findings. Ramaswamy model deals a fair agreement with experimental values in comparison to statistical liquid state PFP model.

Keywords: Isentropic compressibility, Acoustic impedance, Ultrasonic speed, PFP.

Introduction

Ultrasonic studies play a significant role to analyse various thermodynamic properties and to predict the molecular interactions between like and unlike components of liquid mixtures at varying concentration. In the continuation of previously published work¹. This paper is concerned with the study of intermolecular interaction in weakly interacting liquid mixture of 2-butanol and long chain saturated hydrocarbon dodecane. Theoretical interpretation of various physicochemical properties and intermolecular interactions by ultrasonic speed and other acoustical parameters such as isentropic compressibility and acoustic impedance have become a subject of deep interest in past few years. several researchers²⁻⁶ have made a successful attempt to evaluate theoretical ultrasonic speed and other acoustical parameters of different binary liquid mixtures at different temperatures using various liquid state models. PFP⁷⁻¹² model based on non-associated process, Ramaswamy¹³ and Glinski model¹⁴ based on associated process with association constant as adjustable parameter were used to study the extent of interaction between the binary components. McAllister multibody interaction model¹⁵ based on Eyring's theory were used to correlate the theoretical values with experimental findings. Redlich Kister¹⁶ equation was used to determine the binary coefficient and standard deviation using deviation in ultrasonic speed and other acoustical parameters. In this paper an attempt has been made to evaluate the ultrasonic speed, isentropic compressibility and acoustic impedance of binary liquid mixture using different liquid state models from 288.15-318.15K and compared with experimental analysis of Peleteiro¹⁷. The aim of this work to understand the extent of

intermolecular interactions and to estimate the associated and non-associated liquid state models at different temperatures.

Modelling

Prigogine-Flory- Patterson: PFP⁷⁻¹² is a statistical liquid state model based on non-associated process. Ultrasonic speed can be calculated using surface tension of binary liquid mixture from Auerbach relation

$$U = \left(\frac{\sigma}{6.3 \times 10^{-4} \rho_{\text{Mix}}} \right)^{2/3} \quad (1)$$

Where σ is surface tension can be calculated in terms of characteristic surface tension σ^* and reduce surface tension $\tilde{\sigma}(v)$ by the following equation:

$$\sigma = \sigma^* \tilde{\sigma}(v) \quad (2)$$

characteristic surface tension σ^* can be calculated by proposed concept of Patterson and Rastogi of extension of corresponding state theory

$$\sigma^* = K^{1/3} P^{*2/3} T^{*1/3} \quad (3)$$

Where: K , T^* and P^* Boltzmann constant, characteristic temperature and characteristic pressure respectively.

Reduced surface tension $\tilde{\sigma}(v)$ can be calculated by the following equation:

$$\tilde{\sigma}(v) = M v^{5/3} - \frac{(v^{1/3}-1)}{(v^2)} \ln \frac{(v^{1/3}-0.5)}{(v^{1/3}-1)} \quad (4)$$

Where, \tilde{v} is reduced volume which can be calculated from equation (5) by isothermal expansion coefficient (α) and M is adjustable parameter and its values lies in the range $0.25 < M < 0.29$.

$$\tilde{v} = \left[\frac{\alpha T}{3(1+\alpha T)} + 1 \right]^3 \quad (5)$$

Characteristic temperature (T^*) and characteristic pressure (P^*) can be calculated from equation 6 and 7 respectively.

$$T^* = \left[\frac{T(\tilde{v})^{4/3}}{\{(v^{1/3}) - 1\}} \right] \quad (6)$$

$$P^* = \left[\frac{\alpha}{\beta_T} \right] T \tilde{v}^2 \quad (7)$$

Where β_T is isothermal compressibility.

Ramaswamy-Anbananthan model: Ramaswamy¹³ model (associated process) deals with a linear relation between acoustic impedance with the mole fraction. In order to extend the proposed model ultrasonic speed can be calculated by the following equation:

$$U_{RS} = X_1 U_1 + X_2 U_2 + X_{12} U_{12} \quad (8)$$

Where: U_1 , U_2 are ultrasonic speeds of pure component 1 and 2 respectively. U_{12} is ultrasonic speed of associated molecules.

Glinski Model: Glinski¹⁴ proposed a relation, based on an assumption of additivity with volume fraction (Φ) of pure components and associate.

$$U_{GLI} = \frac{U_1 U_2 U_{12}}{U_1 U_{12} \phi_2 + U_2 U_{12} \phi_1 + U_1 U_2 \phi_{12}} \quad (9)$$

Where: ϕ_1 and ϕ_2 are volume fraction of pure components and ϕ_{12} is volume fraction of associate.

Isentropic compressibility: Isentropic compressibility (β_s) can be calculated by Newton – Laplace's equation,

$$\beta_s = \left[\frac{1}{u^2 \rho_{Mix}} \right] \quad (10)$$

ρ_{Mix} is density of binary mixture.

Acoustic impedance: Acoustic impedance of binary liquid mixture is calculated from the following equation

$$Z = U \times \rho_{Mix} \quad (11)$$

McAllister multibody interaction model: McAllister model¹⁵ based on the assumption of Eyring's theory of absolute rate. Which is used to correlate the ultrasonic speed and other acoustical parameter with mole fraction.

McAllister-3- body

$$\ln U = x_1^3 \ln U_1 + 3x_1^2 x_2 \ln U_{A_0} + 3x_1 x_2^2 \ln U_{A_1} + x_2^3 \ln U_2 - \ln[x_1 + x_2 M_2/M_1] + 3x_1^2 x_2 \ln[(2 + M_2/M_1)/3] + 3x_1 x_2^2 \ln[(1 + 2 M_2/M_1)/3] + x_2^3 \ln[M_2/M_1] \quad (12)$$

McAllister-4-body

$$\ln U = x_1^4 \ln U_1 + 4x_1^3 x_2 \ln U_{A_0} + 6x_1^2 x_2^2 \ln U_{A_1} + 4x_1 x_2^3 \ln U_{A_2} + x_2^4 \ln U_2 - \ln[(x_1 + x_2 M_2/M_1)] + 4x_1^3 x_2 \ln[(3 + M_2/M_1)/4] + 6x_1^2 x_2^2 \ln[(1 + M_2/M_1)/2] + 4x_1 x_2^3 \ln[(1 + 3 M_2/M_1)/4] + x_2^4 \ln(M_2/M_1) \quad (13)$$

Where: A_0 , A_1 and A_2 are adjustable parameters. Which were calculated by least square method. M_1 and M_2 are molecular weight of pure liquids.

Results and discussion

Table-1 represents experimental and theoretical ultrasonic speed (U) calculated from various liquid state models for aforesaid liquid mixture along with their percentage deviation from 288.15–318.15K. Theoretical and experimental isentropic compressibility (β_s) along with their percentage deviation is reported in Table-2. Table-3 represents the experimental and theoretical acoustic impedance (Z) along with their percentage deviation at different temperatures. Standard deviation and numerical coefficients calculated from Redlich Kister polynomial are reported in Table-4. Average absolute percentage deviation (AAPD) of ultrasonic speed, isentropic compressibility and acoustic impedance calculated for PFP, Ramaswamy, Glinski, McAllister-3 body model and McAllister-4 body model along with association constant (K_{as}) and adjustable parameters at different temperatures are reported in Table-5, Table-6 and Table-7 respectively.

$$\Delta U = X_1(1 - X_1) \sum_{i=0}^n A_i (1 - X_1)^i \quad (14)$$

Experimental data can be correlated by above Redlich Kister polynomial¹⁶ in terms of mixing function (ΔU). Where A_i is numerical coefficient, which were calculated by multiple regression analysis based least square method and respective ultrasonic properties are represented in term of standard deviations (δU) at different temperatures.

$$\delta U = \left[\sqrt{\sum_{i=1}^k (U_{exp_i} - U_{cal_i})^2 / (N - P)} \right] \quad (15)$$

Where: N is number of experimental points and P is number of adjustable parameters.

A very careful observation of Table-1 reveals that with increase of mole fraction the values of ultrasonic speed calculated from different models decreases and density of binary liquid mixture increases at all temperatures.

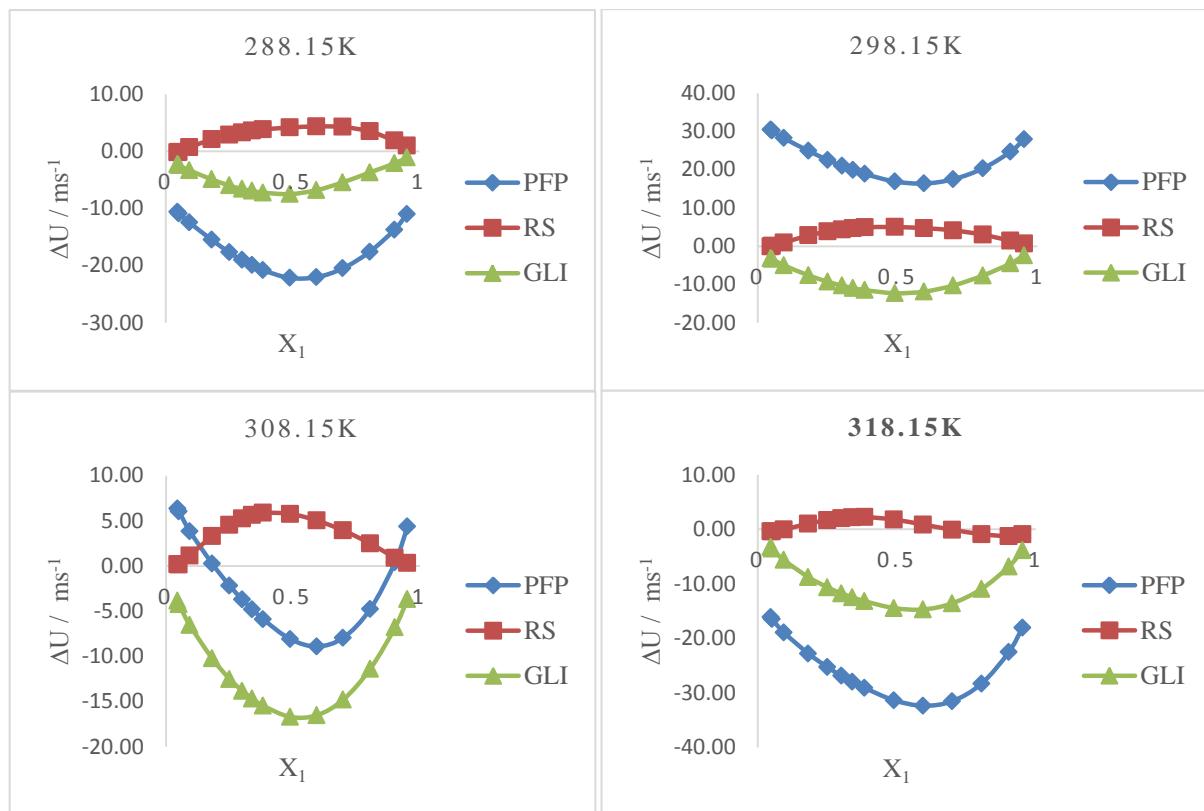


Figure-1: Graphical representation of deviation in ultrasonic speed.

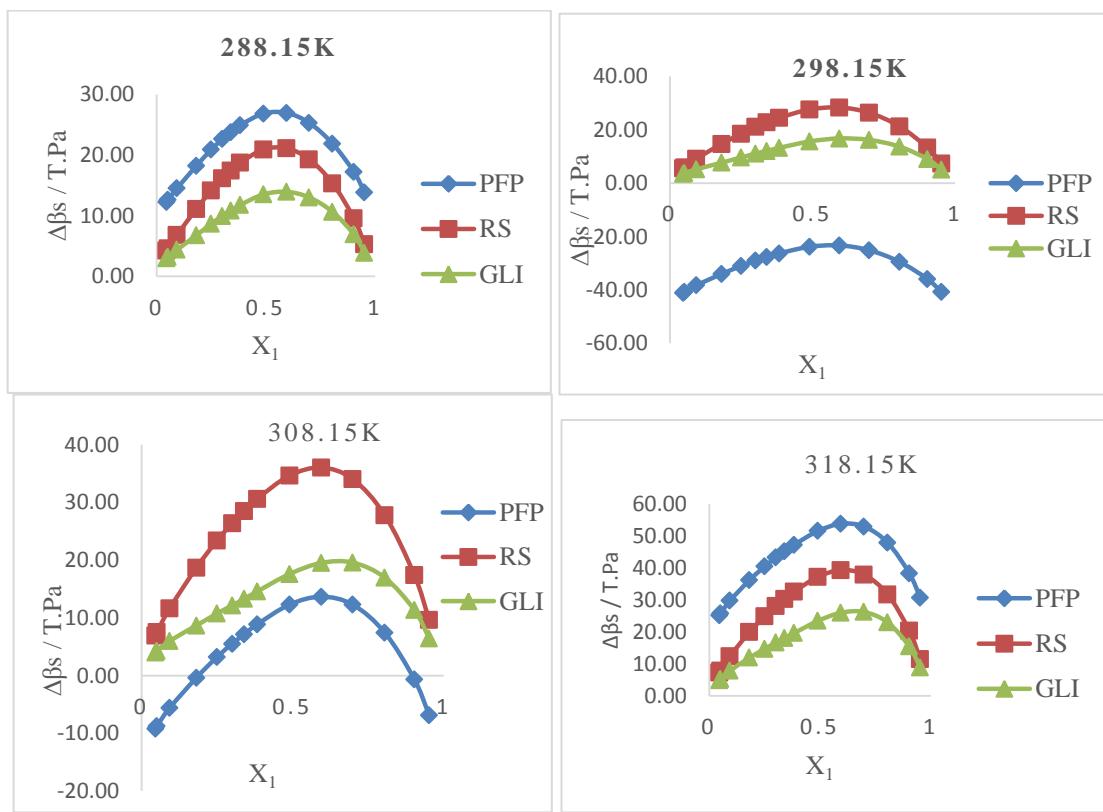


Figure-2: Graphical representation of deviation in isentropic compressibility.

The relative strength of their molecular interactions depends upon the magnitude of percentage deviation and their actual sign. Percentage deviation calculated from Ramaswamy model was very less for entire range of mole fraction in comparison to Glinski and PFP model. Positive deviation in ultrasonic speed show weak molecular interaction¹⁸ between the components of binary system. Magnitude of percentage deviation of concerning models clearly indicate that Ramaswamy model based on association process was found to be more consistent with experimental findings in comparison to Glinski and PFP model. PFP model show more percentage deviation for entire range of mole fraction because the model was developed for γ -meric spherical chain of non-electrolytes¹⁹. Increasing order of percentage deviation in ultrasonic speed is as follows: Ramaswamy < Glinski < PFP. Values of thermal expansion coefficient (α) and isothermal compressibility (β_T) required for PFP model can be calculated in absence of experimental data by the following empirical equation which are already tested by us^{19,20}.

$$\alpha = \frac{75.6 \times 10^{-3}}{T^{1/9} U^{1/2} \rho^{1/3}} K^{-1} \quad (16)$$

$$\beta_T = \frac{1.17 \times 10^{-3}}{T^{4/9} \rho^{4/3} U^2} cm^2 dyne^{-1} \quad (17)$$

Increase in density and non-linear variation of ultrasonic speed with mole fraction as shown in Figure-(1) confirm the solvent-solvent interactions²¹. A perusal of Table-2 reveals that is entropic compressibility (β_S) increases with increase in mole fraction for all the models at different temperatures. Which clearly confirm the inverse relation of ultrasonic speed and isentropic compressibility. Deviation in isentropic compressibility as shown in Figure-2 positively increases with increase in mole fraction of 2-butanol up to a certain limit than decreases. Which indicate that system is very less compact due to the breakup of hydrogen bonds present between alcoholic components²².

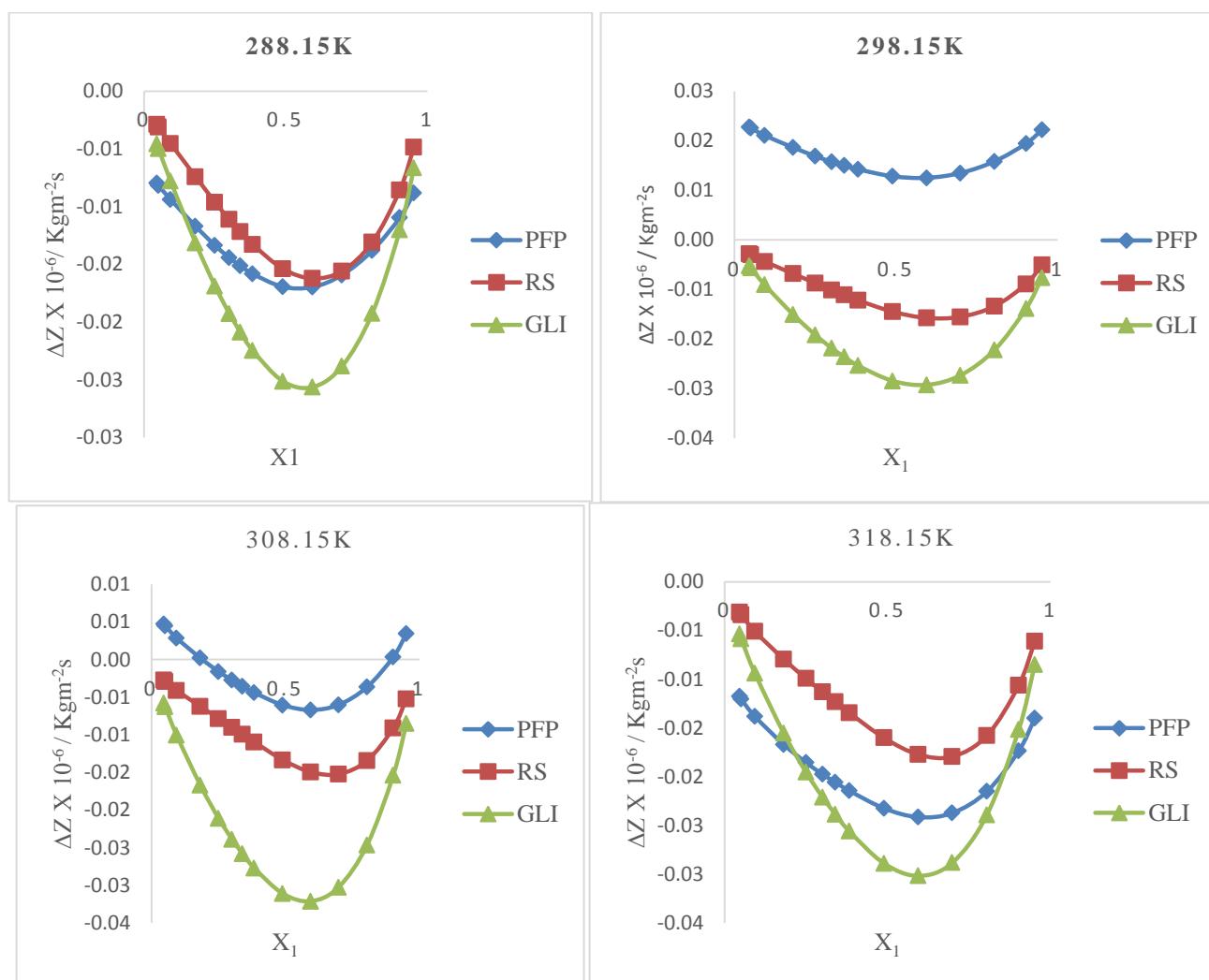


Figure-3: Graphical representation of deviation in acoustic impedance.

Increasing order of percentage deviation in isentropic compressibility is as follows: Glinski < Ramaswamy < PFP. Deviation in acoustic impedance decreases negatively than increases with increase in mole fraction of 2-butanol as shown in Figure-3 for all models at different temperatures. Which indicate the molecular interaction formed by dissociation of hydrogen bonds²³. The result obtained from the discussion of graphical representation support each other. At 298.15K deviation in acoustic impedance calculated by PFP model based on non-association process show positive variation in entire range of mole fraction while other two associated models show negative deviation. Increasing order of percentage deviation in acoustic impedance is as follows: Ramaswamy < Glinski < PFP.

Standard deviations (δU) calculated from Redlich Kister polynomial for mixing function (ΔU) reported in Table-4 varies from $0.24 < \delta < 0.32$ which indicate the excellent correlation between experimental and theoretical findings. AAPD of ultrasonic speed, isentropic compressibility, acoustic impedance calculated for PFP, Ramaswamy and Glinski model reported in Table-5, Table-6 and Table-7 clearly explain Ramaswamy model based on association process gave an excellent result in comparison to Glinski and PFP model based on non-association model, whereas in case of correlation model McAllister-4 body deal a fair agreement with experimental results in comparison to McAllister-3 body model for all the acoustical properties at different temperatures.

Table-1: Experimental, theoretical ultrasonic speed and their % deviation from 288.15-318.15K.

| X ₁ | ρ^{MIX} | U ^{EXP} | U ^{PFP} | U ^{RS} | U ^{GLI} | % Δ^{PFP} | % Δ^{RS} | % Δ^{GLI} |
|----------------|---------------------|------------------|------------------|-----------------|------------------|-------------------------|------------------------|-------------------------|
| T=288.15K | | | | | | | | |
| 0.04602 | 0.7528 | 1312.74 | 1323.31 | 1312.91 | 1315.00 | -0.81 | -0.01 | -0.17 |
| 0.0507 | 0.7529 | 1312.32 | 1323.18 | 1312.47 | 1314.76 | -0.83 | -0.01 | -0.19 |
| 0.09287 | 0.7536 | 1309.26 | 1321.71 | 1308.58 | 1312.58 | -0.95 | 0.05 | -0.25 |
| 0.18128 | 0.7555 | 1302.82 | 1318.31 | 1300.71 | 1307.73 | -1.19 | 0.16 | -0.38 |
| 0.24985 | 0.7572 | 1297.76 | 1315.41 | 1294.89 | 1303.73 | -1.36 | 0.22 | -0.46 |
| 0.30044 | 0.7586 | 1294.05 | 1313.07 | 1290.75 | 1300.64 | -1.47 | 0.25 | -0.51 |
| 0.33974 | 0.7598 | 1291.23 | 1311.13 | 1287.63 | 1298.15 | -1.54 | 0.28 | -0.54 |
| 0.38271 | 0.7612 | 1288.14 | 1308.93 | 1284.30 | 1295.36 | -1.61 | 0.30 | -0.56 |
| 0.48939 | 0.7654 | 1280.62 | 1302.76 | 1276.46 | 1288.09 | -1.73 | 0.33 | -0.58 |
| 0.59429 | 0.7707 | 1273.68 | 1295.69 | 1269.31 | 1280.48 | -1.73 | 0.34 | -0.53 |
| 0.69831 | 0.7773 | 1267.06 | 1287.54 | 1262.79 | 1272.49 | -1.62 | 0.34 | -0.43 |
| 0.80469 | 0.7860 | 1260.19 | 1277.76 | 1256.70 | 1263.89 | -1.39 | 0.28 | -0.29 |
| 0.90245 | 0.7964 | 1253.50 | 1267.23 | 1251.61 | 1255.62 | -1.10 | 0.15 | -0.17 |
| 0.95177 | 0.8028 | 1250.22 | 1261.21 | 1249.23 | 1251.32 | -0.88 | 0.08 | -0.09 |
| T=298.15K | | | | | | | | |
| 0.04602 | 0.7455 | 1273.46 | 1242.97 | 1273.49 | 1276.59 | 2.39 | 0.00 | -0.25 |
| 0.0507 | 0.7455 | 1273.10 | 1242.85 | 1273.02 | 1276.42 | 2.38 | 0.01 | -0.26 |
| 0.09287 | 0.7462 | 1269.82 | 1241.56 | 1268.86 | 1274.80 | 2.23 | 0.08 | -0.39 |
| 0.18128 | 0.7480 | 1263.38 | 1238.47 | 1260.55 | 1270.97 | 1.97 | 0.22 | -0.60 |

| | | | | | | | | |
|---------|--------|---------|---------|---------|---------|------|------|-------|
| 0.24985 | 0.7496 | 1258.36 | 1235.81 | 1254.50 | 1267.63 | 1.79 | 0.31 | -0.74 |
| 0.30044 | 0.7509 | 1254.67 | 1233.69 | 1250.27 | 1264.94 | 1.67 | 0.35 | -0.82 |
| 0.33974 | 0.7522 | 1251.84 | 1231.88 | 1247.10 | 1262.74 | 1.59 | 0.38 | -0.87 |
| 0.38271 | 0.7535 | 1248.76 | 1229.87 | 1243.78 | 1260.21 | 1.51 | 0.40 | -0.92 |
| 0.48939 | 0.7576 | 1241.13 | 1224.20 | 1236.10 | 1253.39 | 1.36 | 0.41 | -0.99 |
| 0.59429 | 0.7627 | 1234.11 | 1217.70 | 1229.37 | 1245.96 | 1.33 | 0.38 | -0.96 |
| 0.69831 | 0.7692 | 1227.66 | 1210.13 | 1223.50 | 1237.91 | 1.43 | 0.34 | -0.83 |
| 0.80469 | 0.7778 | 1221.36 | 1201.00 | 1218.32 | 1229.00 | 1.67 | 0.25 | -0.63 |
| 0.90245 | 0.7882 | 1215.73 | 1191.05 | 1214.30 | 1220.24 | 2.03 | 0.12 | -0.37 |
| 0.95177 | 0.7947 | 1213.24 | 1185.31 | 1212.53 | 1215.62 | 2.30 | 0.06 | -0.20 |

T=308.15K

| | | | | | | | | |
|---------|--------|---------|---------|---------|---------|-------|------|-------|
| 0.04602 | 0.7381 | 1234.92 | 1228.56 | 1234.74 | 1238.76 | 0.52 | 0.01 | -0.31 |
| 0.0507 | 0.7381 | 1234.48 | 1228.44 | 1234.31 | 1238.72 | 0.49 | 0.01 | -0.34 |
| 0.09287 | 0.7387 | 1231.07 | 1227.22 | 1229.90 | 1237.62 | 0.31 | 0.09 | -0.53 |
| 0.18128 | 0.7404 | 1224.51 | 1224.25 | 1221.19 | 1234.74 | 0.02 | 0.27 | -0.84 |
| 0.24985 | 0.7419 | 1219.48 | 1221.66 | 1214.93 | 1231.98 | -0.18 | 0.37 | -1.03 |
| 0.30044 | 0.7432 | 1215.85 | 1219.55 | 1210.59 | 1229.66 | -0.30 | 0.43 | -1.14 |
| 0.33974 | 0.7444 | 1213.01 | 1217.80 | 1207.38 | 1227.69 | -0.40 | 0.46 | -1.21 |
| 0.38271 | 0.7457 | 1209.91 | 1215.81 | 1204.02 | 1225.38 | -0.49 | 0.49 | -1.28 |
| 0.48939 | 0.7496 | 1202.20 | 1210.29 | 1196.43 | 1218.89 | -0.67 | 0.48 | -1.39 |
| 0.59429 | 0.7546 | 1195.02 | 1203.91 | 1189.99 | 1211.53 | -0.74 | 0.42 | -1.38 |
| 0.69831 | 0.7609 | 1188.52 | 1196.45 | 1184.59 | 1203.29 | -0.67 | 0.33 | -1.24 |
| 0.80469 | 0.7694 | 1182.58 | 1187.34 | 1180.09 | 1193.95 | -0.40 | 0.21 | -0.96 |
| 0.90245 | 0.7797 | 1177.79 | 1177.37 | 1176.87 | 1184.58 | 0.04 | 0.08 | -0.58 |
| 0.95177 | 0.7863 | 1175.92 | 1171.57 | 1175.58 | 1179.59 | 0.37 | 0.03 | -0.31 |

T=318.15K

| | | | | | | | | |
|---------|--------|---------|---------|---------|---------|-------|-------|-------|
| 0.04602 | 0.7306 | 1197.08 | 1213.19 | 1197.45 | 1200.36 | -1.35 | -0.03 | -0.27 |
| 0.0507 | 0.7306 | 1196.62 | 1213.10 | 1197.00 | 1200.20 | -1.38 | -0.03 | -0.30 |
| 0.09287 | 0.7312 | 1193.03 | 1211.93 | 1193.08 | 1198.66 | -1.58 | 0.00 | -0.47 |

| | | | | | | | | |
|---------|--------|---------|---------|---------|---------|-------|-------|-------|
| 0.18128 | 0.7326 | 1186.25 | 1209.04 | 1185.24 | 1195.03 | -1.92 | 0.09 | -0.74 |
| 0.24985 | 0.7341 | 1181.20 | 1206.47 | 1179.52 | 1191.84 | -2.14 | 0.14 | -0.90 |
| 0.30044 | 0.7353 | 1177.53 | 1204.38 | 1175.50 | 1189.28 | -2.28 | 0.17 | -1.00 |
| 0.33974 | 0.7364 | 1174.71 | 1202.64 | 1172.50 | 1187.18 | -2.38 | 0.19 | -1.06 |
| 0.38271 | 0.7377 | 1171.59 | 1200.65 | 1169.34 | 1184.76 | -2.48 | 0.19 | -1.12 |
| 0.48939 | 0.7415 | 1163.80 | 1195.14 | 1162.02 | 1178.25 | -2.69 | 0.15 | -1.24 |
| 0.59429 | 0.7462 | 1156.43 | 1188.78 | 1155.58 | 1171.13 | -2.80 | 0.07 | -1.27 |
| 0.69831 | 0.7523 | 1149.84 | 1181.37 | 1149.92 | 1163.42 | -2.74 | -0.01 | -1.18 |
| 0.80469 | 0.7606 | 1143.97 | 1172.25 | 1144.88 | 1154.89 | -2.47 | -0.08 | -0.95 |
| 0.90245 | 0.7709 | 1139.65 | 1162.16 | 1140.92 | 1146.49 | -1.97 | -0.11 | -0.60 |
| 0.95177 | 0.7774 | 1138.24 | 1156.26 | 1139.17 | 1142.06 | -1.58 | -0.08 | -0.34 |

Table-2: Experimental, theoretical isentropic compressibility and their % deviation from 288.15-318.15K.

| X ₁ | βs^{EXP} | βs^{PFP} | βs^{RS} | βs^{GLI} | % $\Delta^{\text{PFP}}_{(\beta s)}$ | % $\Delta^{\text{RS}}_{(\beta s)}$ | % $\Delta^{\text{GLI}}_{(\beta s)}$ |
|----------------|------------------------|------------------------|-----------------------|------------------------|-------------------------------------|------------------------------------|-------------------------------------|
| T=288.15K | | | | | | | |
| 0.04602 | 770.85 | 758.58 | 766.59 | 767.87 | 1.59 | 0.55 | 0.39 |
| 0.0507 | 771.28 | 758.67 | 766.66 | 768.06 | 1.63 | 0.60 | 0.42 |
| 0.09287 | 774.11 | 759.60 | 767.27 | 769.73 | 1.87 | 0.88 | 0.57 |
| 0.18128 | 779.86 | 761.63 | 768.73 | 773.08 | 2.34 | 1.43 | 0.87 |
| 0.24985 | 784.20 | 763.30 | 770.03 | 775.54 | 2.67 | 1.81 | 1.10 |
| 0.30044 | 787.23 | 764.59 | 771.08 | 777.27 | 2.88 | 2.05 | 1.26 |
| 0.33974 | 789.40 | 765.62 | 771.95 | 778.57 | 3.01 | 2.21 | 1.37 |
| 0.38271 | 791.72 | 766.77 | 772.96 | 779.94 | 3.15 | 2.37 | 1.49 |
| 0.48939 | 796.63 | 769.78 | 775.70 | 783.11 | 3.37 | 2.63 | 1.70 |
| 0.59429 | 799.84 | 772.90 | 778.73 | 785.91 | 3.37 | 2.64 | 1.74 |
| 0.69831 | 801.37 | 776.08 | 782.08 | 788.37 | 3.16 | 2.41 | 1.62 |
| 0.80469 | 801.18 | 779.29 | 785.84 | 790.55 | 2.73 | 1.91 | 1.33 |
| 0.90245 | 799.17 | 781.95 | 789.60 | 792.25 | 2.16 | 1.20 | 0.87 |
| 0.95177 | 796.89 | 783.07 | 791.61 | 792.99 | 1.73 | 0.66 | 0.49 |

| T=298.15K | | | | | | | |
|-----------|--------|--------|--------|--------|-------|------|------|
| 0.04602 | 827.19 | 868.27 | 821.64 | 823.70 | -4.97 | 0.67 | 0.42 |
| 0.0507 | 827.60 | 868.38 | 821.67 | 823.93 | -4.93 | 0.72 | 0.44 |
| 0.09287 | 831.12 | 869.39 | 822.00 | 825.97 | -4.60 | 1.10 | 0.62 |
| 0.18128 | 837.62 | 871.66 | 822.97 | 829.99 | -4.06 | 1.75 | 0.91 |
| 0.24985 | 842.49 | 873.52 | 823.99 | 832.88 | -3.68 | 2.20 | 1.14 |
| 0.30044 | 845.93 | 874.95 | 824.88 | 834.87 | -3.43 | 2.49 | 1.31 |
| 0.33974 | 848.39 | 876.11 | 825.67 | 836.34 | -3.27 | 2.68 | 1.42 |
| 0.38271 | 851.05 | 877.38 | 826.61 | 837.87 | -3.09 | 2.87 | 1.55 |
| 0.48939 | 856.87 | 880.74 | 829.33 | 841.30 | -2.79 | 3.21 | 1.82 |
| 0.59429 | 860.85 | 884.21 | 832.55 | 844.14 | -2.71 | 3.29 | 1.94 |
| 0.69831 | 862.59 | 887.76 | 836.28 | 846.43 | -2.92 | 3.05 | 1.87 |
| 0.80469 | 861.88 | 891.34 | 840.63 | 848.23 | -3.42 | 2.46 | 1.58 |
| 0.90245 | 858.39 | 894.33 | 845.12 | 849.38 | -4.19 | 1.55 | 1.05 |
| 0.95177 | 854.83 | 895.60 | 847.56 | 849.78 | -4.77 | 0.85 | 0.59 |
| T=308.15K | | | | | | | |
| 0.04602 | 888.45 | 897.67 | 881.50 | 884.43 | -1.04 | 0.78 | 0.45 |
| 0.0507 | 889.02 | 897.78 | 881.50 | 884.72 | -0.99 | 0.85 | 0.48 |
| 0.09287 | 893.21 | 898.83 | 881.58 | 887.23 | -0.63 | 1.30 | 0.67 |
| 0.18128 | 900.81 | 901.19 | 882.14 | 892.14 | -0.04 | 2.07 | 0.96 |
| 0.24985 | 906.37 | 903.14 | 882.95 | 895.62 | 0.36 | 2.58 | 1.19 |
| 0.30044 | 910.17 | 904.65 | 883.76 | 898.00 | 0.61 | 2.90 | 1.34 |
| 0.33974 | 913.04 | 905.86 | 884.51 | 899.73 | 0.79 | 3.12 | 1.46 |
| 0.38271 | 916.08 | 907.21 | 885.46 | 901.52 | 0.97 | 3.34 | 1.59 |
| 0.48939 | 923.01 | 910.72 | 888.36 | 905.42 | 1.33 | 3.75 | 1.91 |
| 0.59429 | 928.02 | 914.36 | 891.99 | 908.50 | 1.47 | 3.88 | 2.10 |
| 0.69831 | 930.40 | 918.11 | 896.35 | 910.82 | 1.32 | 3.66 | 2.10 |

| | | | | | | | |
|-----------|---------|--------|--------|--------|-------|------|------|
| 0.80469 | 929.38 | 921.94 | 901.58 | 912.41 | 0.80 | 2.99 | 1.83 |
| 0.90245 | 924.53 | 925.18 | 907.09 | 913.17 | -0.07 | 1.89 | 1.23 |
| 0.95177 | 919.76 | 926.61 | 910.12 | 913.29 | -0.74 | 1.05 | 0.70 |
| T=318.15K | | | | | | | |
| 0.04602 | 955.14 | 929.94 | 947.90 | 950.27 | 2.64 | 0.76 | 0.51 |
| 0.0507 | 955.84 | 930.05 | 947.96 | 950.56 | 2.70 | 0.82 | 0.55 |
| 0.09287 | 960.93 | 931.19 | 948.51 | 953.07 | 3.10 | 1.29 | 0.82 |
| 0.18128 | 969.98 | 933.76 | 950.00 | 958.06 | 3.73 | 2.06 | 1.23 |
| 0.24985 | 976.37 | 935.90 | 951.45 | 961.66 | 4.15 | 2.55 | 1.51 |
| 0.30044 | 980.80 | 937.56 | 952.69 | 964.17 | 4.41 | 2.87 | 1.70 |
| 0.33974 | 984.07 | 938.88 | 953.76 | 966.03 | 4.59 | 3.08 | 1.83 |
| 0.38271 | 987.60 | 940.37 | 955.02 | 967.96 | 4.78 | 3.30 | 1.99 |
| 0.48939 | 995.78 | 944.23 | 958.59 | 972.35 | 5.18 | 3.73 | 2.35 |
| 0.59429 | 1002.05 | 948.26 | 962.73 | 976.05 | 5.37 | 3.92 | 2.59 |
| 0.69831 | 1005.35 | 952.40 | 967.44 | 979.12 | 5.27 | 3.77 | 2.61 |
| 0.80469 | 1004.60 | 956.71 | 972.88 | 981.62 | 4.77 | 3.16 | 2.29 |
| 0.90245 | 998.78 | 960.47 | 978.43 | 983.35 | 3.84 | 2.04 | 1.55 |
| 0.95177 | 992.89 | 962.18 | 981.44 | 984.01 | 3.09 | 1.15 | 0.89 |

Table-3: Experimental, theoretical acoustic Impedance and their % deviation from 288.15-318.15K.

| X ₁ | Z ^{exp} X 10 ⁻⁶ | Z ^{PFP} X 10 ⁻⁶ | Z ^{RS} X 10 ⁻⁶ | Z ^{GLI} X 10 ⁻⁶ | %Δ ^{PFP} | %Δ ^{RS} | %Δ ^{GLI} |
|----------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|-------------------|------------------|-------------------|
| T=288.15K | | | | | | | |
| 0.04602 | 0.9882 | 0.9962 | 0.9911 | 0.9928 | -0.81 | -0.29 | -0.46 |
| 0.0507 | 0.9880 | 0.9962 | 0.9911 | 0.9930 | -0.83 | -0.32 | -0.50 |
| 0.09287 | 0.9867 | 0.9961 | 0.9912 | 0.9945 | -0.95 | -0.46 | -0.79 |
| 0.18128 | 0.9842 | 0.9959 | 0.9916 | 0.9974 | -1.19 | -0.75 | -1.34 |
| 0.24985 | 0.9826 | 0.9960 | 0.9922 | 0.9995 | -1.36 | -0.98 | -1.72 |
| 0.30044 | 0.9816 | 0.9961 | 0.9927 | 1.0009 | -1.47 | -1.13 | -1.96 |

| | | | | | | | |
|-----------|--------|--------|--------|--------|-------|-------|-------|
| 0.33974 | 0.9811 | 0.9962 | 0.9932 | 1.0019 | -1.54 | -1.24 | -2.13 |
| 0.38271 | 0.9805 | 0.9964 | 0.9938 | 1.0030 | -1.61 | -1.35 | -2.29 |
| 0.48939 | 0.9802 | 0.9972 | 0.9956 | 1.0054 | -1.73 | -1.57 | -2.56 |
| 0.59429 | 0.9816 | 0.9986 | 0.9978 | 1.0072 | -1.73 | -1.65 | -2.61 |
| 0.69831 | 0.9848 | 1.0008 | 1.0004 | 1.0087 | -1.62 | -1.58 | -2.42 |
| 0.80469 | 0.9905 | 1.0043 | 1.0035 | 1.0097 | -1.39 | -1.32 | -1.94 |
| 0.90245 | 0.9982 | 1.0092 | 1.0068 | 1.0102 | -1.10 | -0.86 | -1.20 |
| 0.95177 | 1.0037 | 1.0125 | 1.0086 | 1.0104 | -0.88 | -0.48 | -0.66 |
| T=298.15K | | | | | | | |
| 0.04602 | 0.9493 | 0.9266 | 0.9521 | 0.9545 | 2.39 | -0.30 | -0.55 |
| 0.0507 | 0.9491 | 0.9266 | 0.9521 | 0.9548 | 2.38 | -0.31 | -0.59 |
| 0.09287 | 0.9475 | 0.9264 | 0.9519 | 0.9565 | 2.23 | -0.46 | -0.95 |
| 0.18128 | 0.9450 | 0.9263 | 0.9518 | 0.9600 | 1.97 | -0.72 | -1.59 |
| 0.24985 | 0.9433 | 0.9264 | 0.9520 | 0.9624 | 1.79 | -0.92 | -2.03 |
| 0.30044 | 0.9422 | 0.9264 | 0.9523 | 0.9640 | 1.67 | -1.07 | -2.31 |
| 0.33974 | 0.9416 | 0.9266 | 0.9526 | 0.9651 | 1.59 | -1.18 | -2.50 |
| 0.38271 | 0.9410 | 0.9267 | 0.9531 | 0.9663 | 1.51 | -1.29 | -2.69 |
| 0.48939 | 0.9403 | 0.9275 | 0.9548 | 0.9687 | 1.36 | -1.54 | -3.02 |
| 0.59429 | 0.9413 | 0.9288 | 0.9570 | 0.9705 | 1.33 | -1.67 | -3.10 |
| 0.69831 | 0.9443 | 0.9308 | 0.9598 | 0.9716 | 1.43 | -1.64 | -2.89 |
| 0.80469 | 0.9500 | 0.9341 | 0.9633 | 0.9722 | 1.67 | -1.41 | -2.34 |
| 0.90245 | 0.9583 | 0.9388 | 0.9671 | 0.9721 | 2.03 | -0.93 | -1.44 |
| 0.95177 | 0.9642 | 0.9420 | 0.9692 | 0.9718 | 2.30 | -0.52 | -0.79 |
| T=308.15K | | | | | | | |
| 0.04602 | 0.9114 | 0.9068 | 0.9142 | 0.9172 | 0.52 | -0.30 | -0.64 |
| 0.0507 | 0.9112 | 0.9067 | 0.9141 | 0.9175 | 0.49 | -0.32 | -0.69 |
| 0.09287 | 0.9094 | 0.9066 | 0.9135 | 0.9195 | 0.31 | -0.45 | -1.11 |

| | | | | | | | |
|---------|--------|--------|--------|--------|-------|-------|-------|
| 0.18128 | 0.9066 | 0.9064 | 0.9128 | 0.9233 | 0.02 | -0.69 | -1.84 |
| 0.24985 | 0.9047 | 0.9063 | 0.9126 | 0.9258 | -0.18 | -0.87 | -2.33 |
| 0.30044 | 0.9036 | 0.9064 | 0.9127 | 0.9275 | -0.30 | -1.00 | -2.64 |
| 0.33974 | 0.9029 | 0.9065 | 0.9129 | 0.9287 | -0.40 | -1.10 | -2.86 |
| 0.38271 | 0.9022 | 0.9066 | 0.9132 | 0.9299 | -0.49 | -1.21 | -3.07 |
| 0.48939 | 0.9012 | 0.9073 | 0.9145 | 0.9323 | -0.67 | -1.48 | -3.45 |
| 0.59429 | 0.9017 | 0.9084 | 0.9167 | 0.9338 | -0.74 | -1.66 | -3.56 |
| 0.69831 | 0.9043 | 0.9104 | 0.9196 | 0.9346 | -0.67 | -1.69 | -3.35 |
| 0.80469 | 0.9099 | 0.9135 | 0.9233 | 0.9345 | -0.40 | -1.48 | -2.71 |
| 0.90245 | 0.9184 | 0.9180 | 0.9275 | 0.9337 | 0.04 | -0.99 | -1.68 |
| 0.95177 | 0.9246 | 0.9212 | 0.9298 | 0.9331 | 0.37 | -0.57 | -0.92 |

T=318.15K

| | | | | | | | |
|---------|--------|--------|--------|--------|-------|-------|-------|
| 0.04602 | 0.8746 | 0.8864 | 0.8777 | 0.8800 | -1.35 | -0.36 | -0.62 |
| 0.0507 | 0.8743 | 0.8863 | 0.8777 | 0.8802 | -1.38 | -0.39 | -0.67 |
| 0.09287 | 0.8723 | 0.8861 | 0.8774 | 0.8817 | -1.58 | -0.58 | -1.08 |
| 0.18128 | 0.8691 | 0.8858 | 0.8770 | 0.8846 | -1.92 | -0.91 | -1.79 |
| 0.24985 | 0.8671 | 0.8856 | 0.8770 | 0.8866 | -2.14 | -1.15 | -2.25 |
| 0.30044 | 0.8659 | 0.8856 | 0.8772 | 0.8880 | -2.28 | -1.31 | -2.55 |
| 0.33974 | 0.8651 | 0.8856 | 0.8774 | 0.8889 | -2.38 | -1.42 | -2.76 |
| 0.38271 | 0.8643 | 0.8857 | 0.8777 | 0.8899 | -2.48 | -1.56 | -2.96 |
| 0.48939 | 0.8629 | 0.8861 | 0.8789 | 0.8918 | -2.69 | -1.86 | -3.35 |
| 0.59429 | 0.8630 | 0.8871 | 0.8807 | 0.8931 | -2.80 | -2.05 | -3.50 |
| 0.69831 | 0.8651 | 0.8888 | 0.8830 | 0.8939 | -2.74 | -2.07 | -3.33 |
| 0.80469 | 0.8701 | 0.8917 | 0.8859 | 0.8941 | -2.47 | -1.81 | -2.75 |
| 0.90245 | 0.8785 | 0.8959 | 0.8892 | 0.8937 | -1.97 | -1.21 | -1.73 |
| 0.95177 | 0.8848 | 0.8989 | 0.8910 | 0.8933 | -1.58 | -0.69 | -0.96 |

Table-4: Coefficients and standard deviation of Redlich Kister polynomial.

| T/K | A ₀ | A ₁ | A ₂ | A ₃ | δU |
|--------|----------------|----------------|----------------|----------------|------|
| 288.15 | -6.7840 | 0.8589 | -9.5917 | 15.2087 | 0.38 |
| 298.15 | -14.6155 | -6.6252 | -15.1473 | 17.7979 | 0.36 |
| 308.15 | -20.9362 | -12.5154 | -21.7222 | 18.1055 | 0.32 |
| 318.15 | -25.2409 | -15.1511 | -25.8856 | 10.6701 | 0.24 |

Table-5: Average absolute % deviation of ultrasonic speed along with association constant (K_{as}) and adjustable parameter (U_{AB}) from 288.15-318.15K.

| T/K | K _{as} | U _{AB} | AAPD | | | | |
|--------|-----------------|-----------------|------------------|-----------------|------------------|-------------------|-------------------|
| | | | U ^{PFP} | U ^{RS} | U ^{GLI} | U ^{Mc-3} | U ^{Mc-4} |
| 288.15 | 0.02 | 1250.25 | 1.30 | 0.20 | 0.37 | 0.07 | 0.03 |
| 298.15 | 0.03 | 1225.25 | 1.83 | 0.24 | 0.63 | 0.06 | 0.03 |
| 308.15 | 0.04 | 1225.25 | 0.40 | 0.26 | 0.90 | 0.05 | 0.03 |
| 318.15 | 0.03 | 1185.25 | 2.13 | 0.10 | 0.82 | 0.03 | 0.12 |

Table-6: Average absolute % deviation of isentropic compressibility along with association constant (K_{as}) and adjustable parameter (βs_{AB}) from 288.15-318.15K.

| T/K | k _{as} | βs _{AB} | AAPD | | | | |
|--------|-----------------|------------------|-------------------|------------------|-------------------|--------------------|--------------------|
| | | | βs ^{PFP} | βs ^{RS} | βs ^{GLI} | βs ^{Mc-3} | βs ^{Mc-4} |
| 288.15 | 0.02 | 778.65 | 2.61 | 1.67 | 1.09 | 0.14 | 0.04 |
| 298.15 | 0.03 | 835.65 | 3.70 | 2.06 | 1.19 | 0.17 | 0.04 |
| 308.15 | 0.04 | 889.23 | 0.80 | 2.44 | 1.29 | 0.21 | 0.04 |
| 318.15 | 0.03 | 972.67 | 4.19 | 2.46 | 1.60 | 0.24 | 0.03 |

Table-7: Average absolute % deviation of acoustic impedance along with association constant (K_{as}) and adjustable parameter (Z_{AB}) from 288.15-318.15K.

| T/K | K _{as} | Z _{AB} X10 ⁻⁶ | AAPD | | | | |
|--------|-----------------|-----------------------------------|------------------|-----------------|------------------|-------------------|-------------------|
| | | | Z ^{PFP} | Z ^{RS} | Z ^{GLI} | Z ^{Mc-3} | Z ^{MC-4} |
| 288.15 | 0.02 | 1.00 | 1.30 | 1.00 | 1.61 | 0.04 | 0.02 |
| 298.15 | 0.03 | 0.96 | 1.80 | 1.00 | 1.92 | 0.03 | 0.03 |
| 308.15 | 0.04 | 0.92 | 0.40 | 0.99 | 2.20 | 0.04 | 0.03 |
| 318.15 | 0.03 | 0.88 | 2.13 | 1.24 | 2.16 | 0.05 | 0.03 |

Conclusion

On the basis of above analysis, it can be concluded that ultrasonic speed, isentropic compressibility and acoustic impedance computed for different models at different temperatures provide a way to understand the molecular interaction between the binary components. Ramaswamy and Glinski model based on association process gave more reliable results in comparison to PFP model based on non-associated model and are helpful in predicting the internal structure of molecular complexes during mixing through the fitted values of ultrasonic speed and other acoustical parameters.

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