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Ultrasonic Studies of Molecular Interactions in Polymer Solution of the Polyisobutylene (PIB) and Benzene

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Summary

Ultrasonic studies of intermolecular interactions in the polymer solution of poly isobutylene (PIB) and Benzene have been done at 40 °C using ultrasonic velocity, density and refractive index data taken from literature. Several acoustic parameters such as acoustic impedance, isothermal compressibility, molar sound velocity, molar adiabatic compressibility, internal pressure, free volume, van der Waal constants, molar cohesive energy, molecular radius and relaxation time have been studied. A large number of thermo-dynamical parameters such as available volume, geometrical volume, intermolecular free length, relative association, surface tension, molar refraction, pseudo-Gruneisen parameter, Debye temperature, diffusion constant, coefficient of thermal conductivity, latent heat of melting and electronic polarisability have also been evaluated. Several thermo-elastic parameters such as Young modulus, shear modulus, bulk modulus and Poisson ratio are also determined. Schaaff's collision factor theory, Nomoto's relation, Van Dael-Vangeel relation, impedance dependence relation and ideal mixing relation have been used to predict the values of ultrasonic velocities in the system under study. The obtained results have been compared with the experimental results as available in literature. Present investigation of the polymer solution provides a deep insight into the nature, type and strength of intermolecular interactions prevalent in it. The non-ideal behaviour of the solution has been explained in terms of its composition and variation of its acoustical and thermo-dynamical parameters.

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1. Introduction

Ultrasonic studies in polymers solutions [1, 2, 3] and in solid polymers [4, 5] have been subjects of the extensive research activity in recent years. Ultrasonic measurements provide considerable information about various properties of the polymer solutions. Polyisobutylene (PIB) is chosen for the present investigation, because of its industrial applications [6]. Polyisobutylene (PIB) commonly known as synthetic rubber, has properties of special interest as it is gas impermeable. i.e it is only rubber that can hold air for long periods of time.

Varada Rajulu *et al.* [6] experimentally measured the ultrasonic velocity, density and refractive index of Polyisobutylene (PIB) in Benzene at 40 °C. They discussed the variation of the excess compressibility and excess space filling factor of the polymer solution with change in mole fraction of Polyisobutylene (PIB). The obtained results reveal interaction between the molecules of benzene and PIB. A review of literature [1, 2, 3, 4, 5, 6] suggested that little work has been reported for the properties of PIB in solution form. In present article several acoustical and thermo-dynamical parameters of the polymer solution of PIB and Benzene at 40 °C are investigated. The study determines the variation of large number of thermo-acoustical parameters and with change in mole fraction of PIB in benzene. Some thermo-elastic parameters of the system are also evaluated. The present investigations provide a deep insight into the nature, type and strength of intermolecular interactions prevalent in the system under study.

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2. Theory

Experimental value of ultrasonic velocity U, density d and refractive index n_D w.r.t. D line of sodium have been taken from literature [6]. Several researchers have reported that acoustical parameters are a versatile tool to investigate molecular interactions in pure liquid and binary mixtures [7, 8, 9, 10, 11]. Using experimental U, d and n_D values several acoustical and thermodynamical parameters for the polymer solution of PIB and Benzene are determined. The standard relations as given below are used to evaluate various parameters.

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Longitudinal wave velocity U_l and shear wave velocity U_S are calculated as

$$U_l = \frac{1}{\sqrt{dK_T \frac{1+\sigma}{3(1-\sigma)}}}, \quad (1)$$

$$U_S = \frac{1}{\sqrt{dK_T \frac{2(1+\sigma)}{3(1-2\sigma)}}}, \quad (2)$$

where K_T is isothermal compressibility and σ is Poisson ratio. Young's modulus E, shear modulus G, bulk modulus K and average sound velocity U_m are calculated using standard relations [9] as

$$E = U_l^2 d, \quad (3)$$

$$G = U_S^2 d, \quad (4)$$

$$K = \frac{3E - 4G}{3}, \quad (5)$$

$$\sigma = \frac{3K - 2G}{6K + 2G}, \quad (6)$$

$$U_m = \sqrt{U_l^2 - 4U_S^2/3}. \quad (7)$$

Available volume V_a, geometrical volume B, Eykmann constant E_c, molecular refraction M_R, intermolecular free length L_f, relative association (R.A.), free volume V_f, internal pressure P_i, van der Waal's pressure constant a, co-volume b, molar cohesive energy ΔH, coefficient of viscosity η, relaxation time τ, diffusion constant D_i specific acoustic impedance Z, isothermal compressibility K_T, specific heat ratio γ, Debye temperature θ_D, thermal expansivity α, pseudo Gruneisen parameter Γ, coefficient of thermal conductivity k', molecular radius r_m, latent heat of melting ΔH_m, electronic polarisability α_e, surface tension σ_{ST} and ultrasonic velocity values using collision factor theory U_{CFT} are calculated using standard relations taken from literature [10, 11, 12]. Molar sound velocity R and molar adiabatic compressibility W are calculated using the standard relation reported by Singh *et al.* [13] as given hereafter

$$V_a = V\left(1 - \frac{U}{U_\infty}\right), \quad (8)$$

where, $U_\infty = 1600$ m/s and V is molar volume.

$$B = \frac{4}{3}\pi r_m^3 N, \quad (9)$$

where

$$r_m = \sqrt[3]{\frac{3V}{16\pi N}\left[1 - \frac{\gamma RT}{MU^2}\left(\sqrt{1 + \frac{MU^2}{3RT}} - 1\right)\right]}$$

is the molecular radius and N is the Avogadro number,

$$E_C = \frac{n_D^2 - 1}{(n_D + 0.4)d}, \quad (10)$$

$$M_R = \frac{n_D^2 - 1}{n_D^2 + 2}V, \quad (11)$$

$$L_f = \frac{2V_a}{Y_S}, \quad (12)$$

where $Y_S = (36\pi N V_0^2)^{1/3}$ is molar surface area.

$$\mathrm{R.A.} = \left(\frac{L_f}{L_f'}\right)^2, \quad (13)$$

where L_f' is the intermolecular free length found by using ultrasonic velocity values.

$$b = \frac{M}{d}\left[1 - \frac{RT}{MU^2}\left(\sqrt{1 + \frac{MU^2}{3RT}} - 1\right)\right], \quad (14)$$

$$V_f = V - b, \quad (15)$$

$$P_i = \frac{B'RT}{\sqrt[3]{V_f - V^2}}, \quad (16)$$

where $B' = 1.76$ and R is the universal gas constant.

$$a = P_i V^2, \quad (17)$$

$$\Delta H = P_i v, \quad (18)$$

$$\eta = \frac{MU}{KV_f}, \quad (19)$$

where K is $4.28 \cdot 10^9$.

$$\tau = \eta K_s, \quad (20)$$

where K_s is the adiabatic compressibility.

$$D_i = \frac{k d_0^2 \theta_D}{96h}, \quad (21)$$

where d_0 is the molecular diameter, h is planck's constant, θ_D is Debye temperature and k is Boltzmann's constant.

$$Z = Ud, \quad (22)$$

$$K_s = \frac{1}{u^2 d}, \quad (23)$$

$$R = \frac{M}{d}\sqrt[3]{U}, \quad (24)$$

$$W = \frac{M}{d}\frac{1}{\sqrt[7]{K_s}}, \quad (25)$$

$$K_T = \frac{1.71 \cdot 10^{-3}}{T^{4/9} U^2 d^{4/3}}, \quad (26)$$

$$\gamma = \frac{K_T}{K_S}, \quad (27)$$

$$\theta_D = \frac{h}{k}\sqrt[3]{\left(\frac{9N}{4\pi V}\right)\Big/\left(\frac{1}{U^3 l} + \frac{1}{U^3 s}\right)}, \quad (28)$$

$$a = \frac{75.6 \cdot 10^{-3}}{T^{1/9} U^{1/2} d^{1/3}}, \quad (29)$$

where T is temperature in Kelvin.

$$\Gamma = \frac{\gamma - 1}{Ta}, \quad (30)$$

$$k' = 2.8k\left(\frac{dN}{M}\right)^{2/3}\gamma^{1/3}U, \quad (31)$$

$$\Delta H_m = \frac{9M}{128}\left(\theta_D d_0 \frac{k}{h}\right)^2, \quad (32)$$

Table I. Ultrasonic velocity of polymer solution of PIB + Benzene at 40 °C.

X	U	U^{im}	U_{CFT}	U_N	U_V	U_Z
X1	1228	1226	1495	1232	1203	1226
X2	1228	1228	1491	1239	1181	1228
X3	1230	1229	1499	1245	1159	1229
X4	1231	1230	1501	1252	1136	1230
X5	1238	1234	1463	1265	1089	1234
X6	1242	1236	1507	1272	1065	1236
X7	1247	1238	1510	1278	1044	1238

Table II. Percentage error for theoretical values of ultrasonic velocity calculated from ideal mixture relation, CFT, Nomoto's relation, Van Dael-Vangeel relation and impedance dependence relation for polymer solution of PIB + Benzene at 40 °C.

U^{im}	U_{CFT}	U_N	U_V	U_Z
0.16	-21.74	-0.33	2.04	0.16
0.00	-21.42	-0.90	3.83	0.00
0.08	-21.87	-1.22	5.77	0.08
0.08	-21.93	-1.71	7.72	0.08
0.32	-18.17	-2.18	12.04	0.32
0.48	-21.34	-2.42	14.25	0.48
0.72	-21.09	-2.49	16.28	0.72

where k is Boltzmann constant and h is Planck's constant.

$$a_e = \frac{3}{4\pi V}\frac{M_{\text{eff}}}{d}\frac{n^2-1}{n^2+1}, \tag{33}$$

$$\sigma_{ST} = 10^{-4}U^{3/4}dT^{1/3}. \tag{34}$$

Ultrasonic velocity values are calculated using ideal mixing relation U^{im}, Nomoto's relation U_N, Van Dael-Vangeel relation U_V and impedance dependence relation U_Z as reported in literature [14].

$$U_{\text{CFT}} = U_\infty\left(X_1S_1 + X_2S_2\right)\frac{X_1B_1 + X_2B}{V}, \tag{35}$$

$$U^{\text{im}} = \sum_1^2 X_iU_i, \tag{36}$$

$$U_N = \left(\frac{X_1R_1 + X_2R_2}{X_1V_1 + X_2V_2}\right)^3, \tag{37}$$

$$U_V = \left(X_1M_1 + X_2M_2\right)\left(\frac{X_1}{M_1U_1^2} + \frac{X_2}{M_2U_2^2}\right)^{-1/2}, \tag{38}$$

$$U_Z = \frac{X_1Z_1 + X_2Z_2}{X_1d_1 + X_2d_2}. \tag{39}$$

3. Result

The results obtained for PIB+ Benzene polymers solution at mole fraction X of the PIB at $X_1 = 0.0082$, $X_2 = 0.0171$, $X_3 = 0.0268$, $X_4 = 0.0376$, $X_5 = 0.00627$, $X_6 = 0.0775$ and $X_7 = 0.0942$ are presented in the Figures 1 to 12. Ultrasonic velocity as determined using various theoretical formulae and there %-error are reported in Tables I and II. All the results are in SI units except stated otherwise.

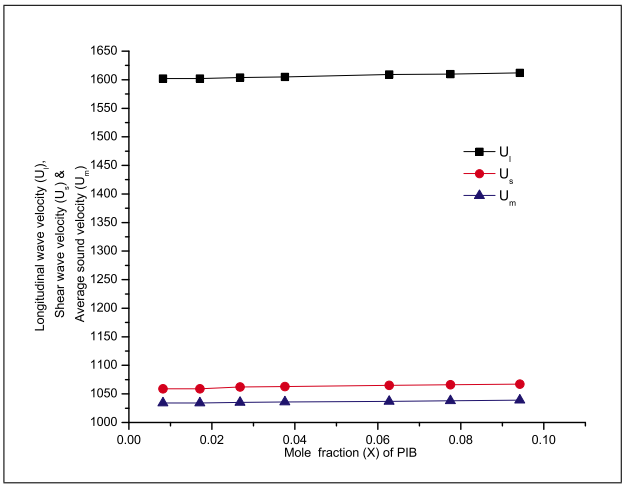


Figure 1. Variation of U_l, U_s and U_m with mole fraction X of PIB.

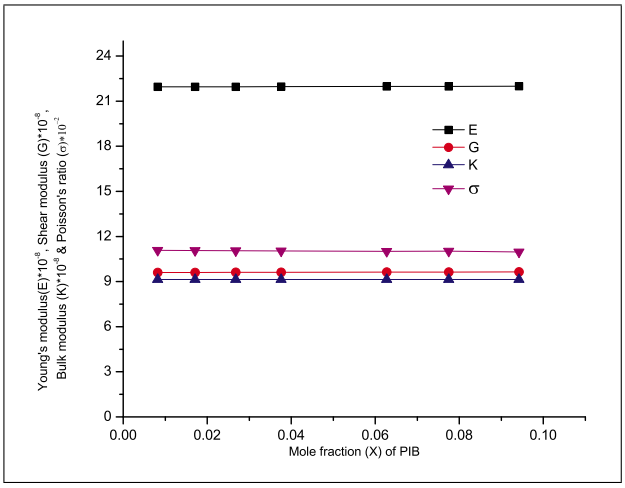


Figure 2. Variation of E, G, K and σ with mole fraction X of PIB.

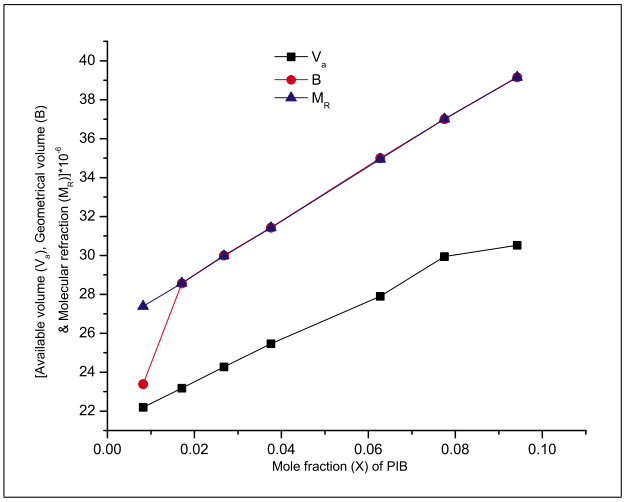


Figure 3. Variation of V_a, B and M_R with mole fraction X of PIB.

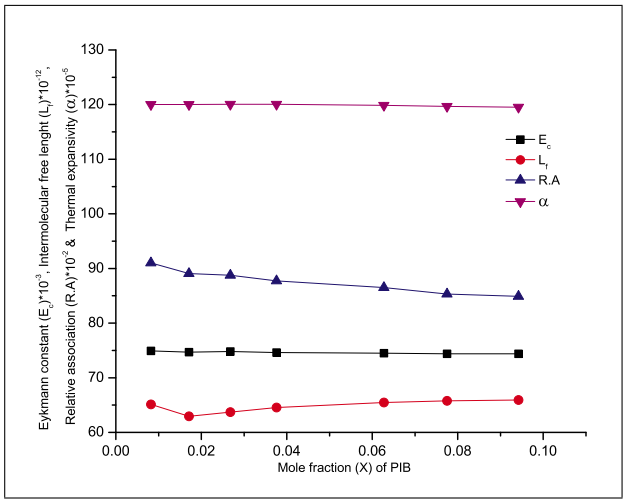


Figure 4. Variation of E_c, L_f, R.A. and α with mole fraction X of PIB.

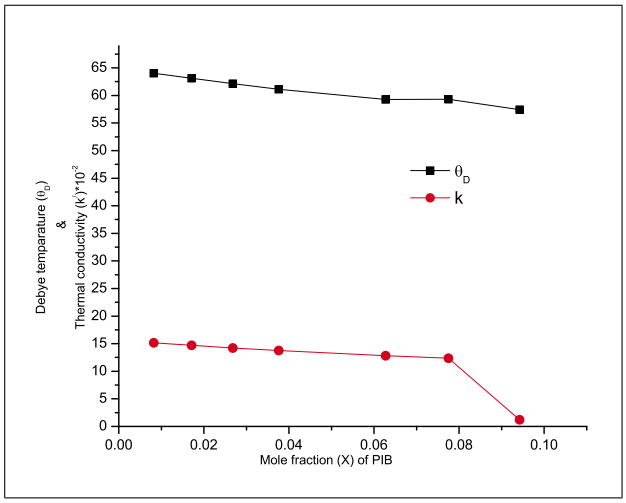


Figure 5. Variation of σ_D and k with mole fraction X of PIB.

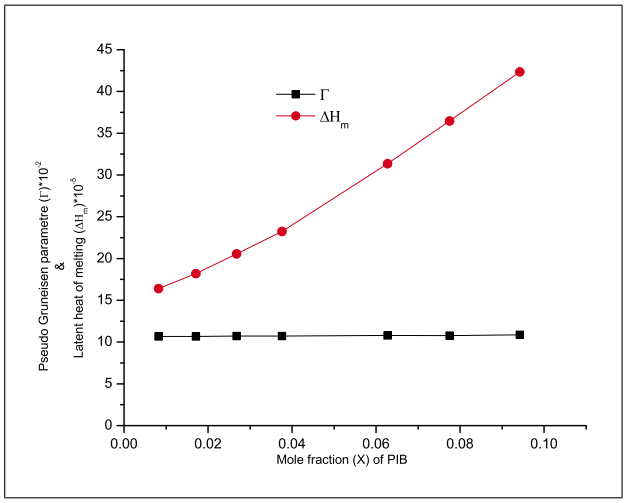


Figure 6. Variation of Γ and ΔH_m with mole fraction X of PIB.

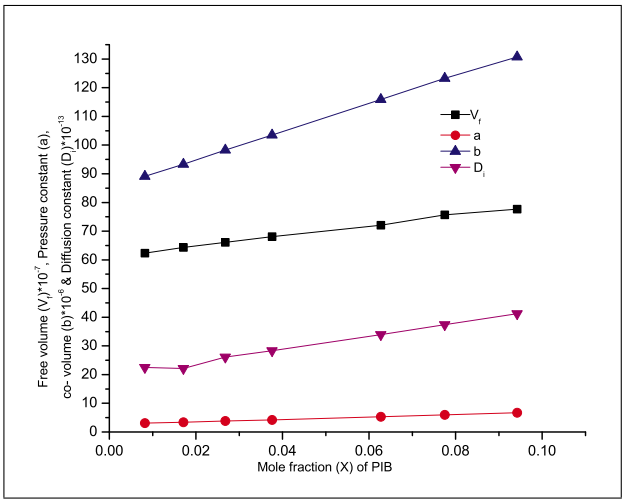


Figure 7. Variation of V_f, a, b and D_i with mole fraction X of PIB.

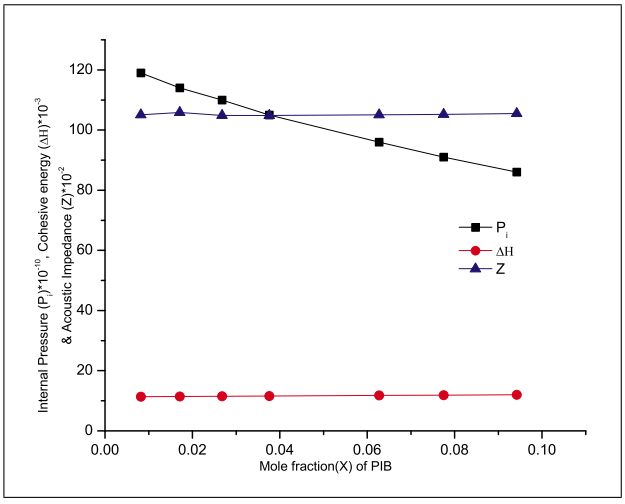


Figure 8. Variation of P_i, ΔH and Z with mole fraction X of PIB.

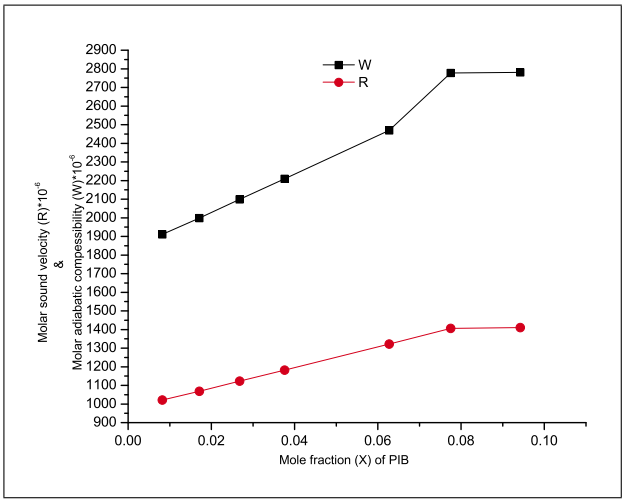


Figure 9. Variation of R and W with mole fraction X of PIB.

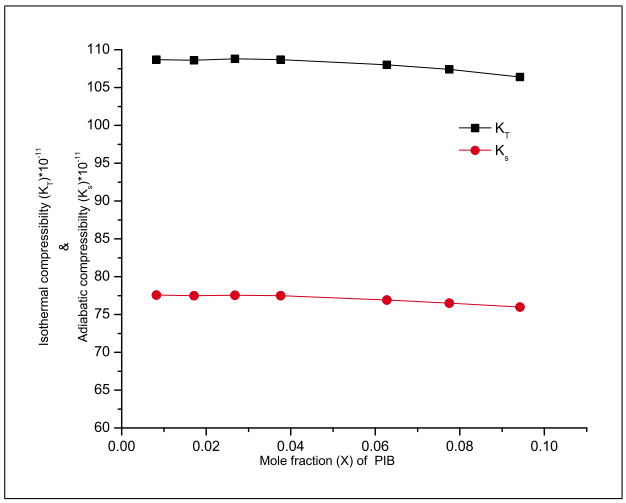


Figure 10. Variation of K_T and K_s with mole fraction X of PIB.

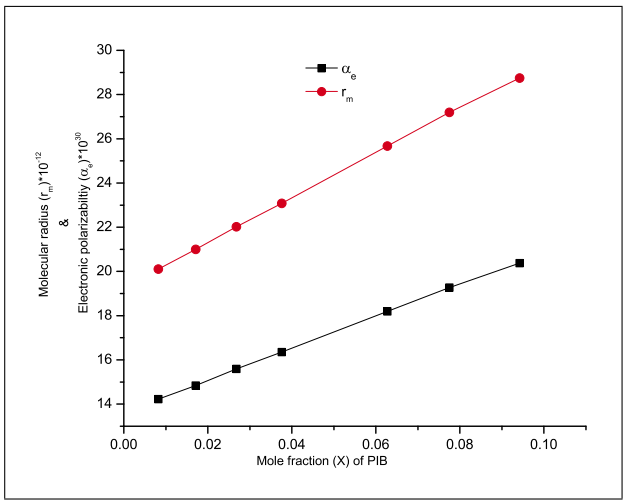


Figure 11. Variation of r_m and α_e with mole fraction X of PIB.

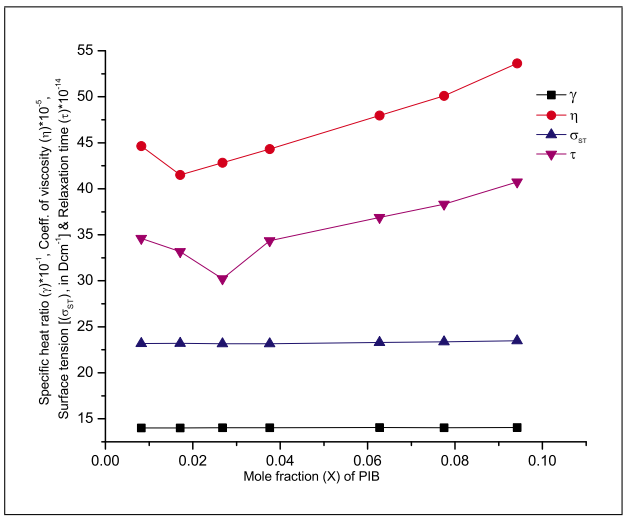


Figure 12. Variation of γ, η, σ and τ with mole fraction X of PIB.

4. Discussion

The perusal of Tables I and II indicate that Collision factor theory U_{CFT} and Nomoto's relation U_N overestimate the ultrasonic velocity values, whereas Van Dael-Vangeel relation U_V underestimates these for the system. Using ideal mixing relation U^{im} and impedance dependence U_Z relation a good estimate of ultrasonic velocities in the polymers solution under study is obtained.

The perusal of Figure 1 and Figure 2 indicate that longitudinal wave velocity U_l, shear wave velocity U_s, average sound velocity U_m, Young's modulus E, shear modulus G bulk modulus K and Poisson's ratio σ are not much affected as the mole fraction of PIB increases from X_1 to X_7.

The calculated value of available volume V_a, geometrical volume B, molecular refraction M_R are reported in Figure 3. These parameters show a regular increase in their values as the mole fraction of the PIB is increased from X_1 to X_7 in the solution. The Ekymann constant E_c) reports a constant value of about $7.4 \cdot 10^{-4}$ whereas thermal expansivity a report slight decrease in its value (Figure 4). This trend of the variation of these parameters is as expected since addition of long chain molecules of the PIB to the system enhances dispersive force in it. This is further confirmed by the trend of variation of relative association R.A. (Figure 4), which report slight decrease in its values with rise in mole fraction of PIB in the system. The dispersal forces are weak in nature as is confirmed by almost constant behavior of intermolecular free length L_f (Figure 4) having value of about 65 pm in the system.

The variation of solid state parameters such as Debye temperature θ_D, pseudo-Gruneisen parameter Γ, coefficient of the thermal conductivity k' and Latent heat of melting ΔH_m with mole fraction X of PIB are reported in Figure 5 and Figure 6 respectively. θ_D and k' show a decrease in their values, whereas Γ and ΔH_m show an opposite trend, with addition of the PIB the solution.

The variation of fupmanyuree volume V_f, van der Waal's pressure constant a, co-volume b and diffusion constant D_i are reported in the Figure 7. V_f, a and b show distinct increasing trend pointing to addition of long chain molecules of the PIB in the system. The increase in diffusion constant D_i values with rise in mole fraction of PIB in the system points to increased diffusion of the benzene molecules in the interstitial space of PIB, leading to clathrate formation in the system. This fact is confirmed by almost constant value of the molar cohesive energy ΔH (Figure 8) and decreasing trend of the internal pressure P_i (Figure 8) with rise of the mole fraction of the PIB from X_1 to X_7.

The variation of several acoustical parameters such as molar adiabatic compressibility W, molar sound velocity R, adiabatic compressibility K_s and isothermal compressibility K_T as a function of mole fraction of PIB are presented in Figures 9 and 10 respectively. The perusal of the Figure 9 points that as the mole fraction of the PIB in polymers solution increased from X_1 to X_7, W and R show an increase in their values, pointing to existence of the

weak intermolecular association among the solute-solvent molecules. The value of the K_s and K_T remain constant at low concentration PIB in solution as the concentration of PIB in solution increases, their value decreases slightly. The decrease in the value of the K_s and K_T confirms the lesser availability of the free volume V_f (Figure 7). The increase in r_m value with addition of PIB in the polymers solution is as expected, as long chain PIB molecules are being added to the system.(Figure 11). This trend of the weak association among constituent molecules of the system as pointed out by almost constant magnitude of the Z (Figure 8) with rise in mole fraction of PIB in the system is further confirmed by the slight increase in the values of the electronic polarisability a_e (Figure 11) and coefficient of viscosity η (Figure 12) with such a change. The constant value of the molar cohesive energy ΔH (Figure 8) also provides the quantitative measure of the associative interaction in the polymer solution.

The surface tension σ_{ST} and ratio of specific heat γ remain unaffected with molecular changes in the system and the relaxation time τ also shows decrease in its value at low concentration of PIB in solution as the concentration of PIB increase in the solution it shows regular increase in its value. This trend of variation is presented in Figure 12.

5. Conclusion

Ultrasonic investigation in polymer solution of PIB and Benzene provide a qualitative and quantitative measure of solute-solvent interactions in the system. However collision factor theory (U_{CFT}), Nomoto's relation (U_N) and Van Dael-Vangeel relation (U_V) fail to predict the ultrasonic velocities in this system. It is also pointed out that the variation of the acoustical and thermo dynamical parameters indicate the correct nature, type and strength of intermolecular interactions among the constitutes of the PIB + Benzene solution.

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