

Synthesis, Speed of Ultrasound and Associated Acoustical Parameters of Epoxy Acrylate of 9,9'-bis (4-Hydroxy Phenyl) Anthrone-10 Solutions

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ABSTRACT: Density (ρ), viscosity (η), and speed of ultrasound (U) (2 MHz) of pure solvents (chloroform, THF, and 1,4-dioxane) and solutions of epoxy acrylate of 9,9'-bis(4-hydroxy phenyl) anthrone-10 (EAAN) have been investigated at 303, 308, and 313 K. Specific acoustical impedance (Z), isentropic compressibility (κ_s), intermolecular free path length (L_f), classical absorption coefficient ($(\alpha/f^2)_{cl}$), and viscous relaxation time (τ) have been determined from ρ , η , and U data and are correlated with concentration. Z , $(\alpha/f^2)_{cl}$, and τ increased with C and decreased with T , while κ_s and L_f decreased

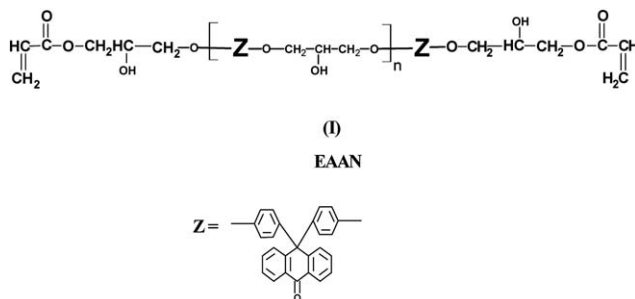
with C and increased with T in the solvent systems studied. A fairly good to excellent correlation between a given parameter and concentration is observed in solvent systems studied. Linear increase or decrease of acoustical parameters with concentration and temperature indicated existence of strong molecular interactions. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1304–1310, 2011

Key words: speed of ultrasound; density; viscosity; acoustical parameters; molecular interactions; epoxy acrylate

INTRODUCTION

The measurements of density (ρ), viscosity (η), and speed of ultrasonic and associated acoustical parameters have become useful tools, because they furnish value added information about molecular structure, size, shape, molecular packing, molecular motion as well as the strength of specific and nonspecific interactions between components of the liquid mixture, electrolyte, and polymer solutions. Molecular interactions are of almost importance for processes involving polymer production and uses.^{1–9}

Unsaturated polyesters are becoming increasingly popular because of their low cost, ease of use, and versatility.¹⁰ To our knowledge, no work has been reported on synthesis, speed of ultrasound, and associated parameters of epoxy acrylate of 9,9'-bis (4-hydroxy phenyl) anthrone-10, which encouraged us to investigate the effect of concentration, temperature, and solvents on molecular interactions in epoxy acrylate solutions (I).



EXPERIMENTAL

Materials

Chemicals and solvents used in this study were of laboratory grade and purified according to literature methods.¹¹ Epoxy resin of 9,9'-bis (4-hydroxy phenyl) anthrone-10 (EAN) (Epoxy equivalent = 910) was synthesized and purified according to our recent publication.¹²

Synthesis of epoxy acrylate of 9,9'-bis (4-hydroxy phenyl) anthrone-10

To a 500-mL three-necked flask equipped with a mechanical stirrer, a condenser and a thermometer was placed in a thermostat and were added 0.01 mol (9.52 g) epoxy resin in 30 mL 1,4-dioxane, 0.02

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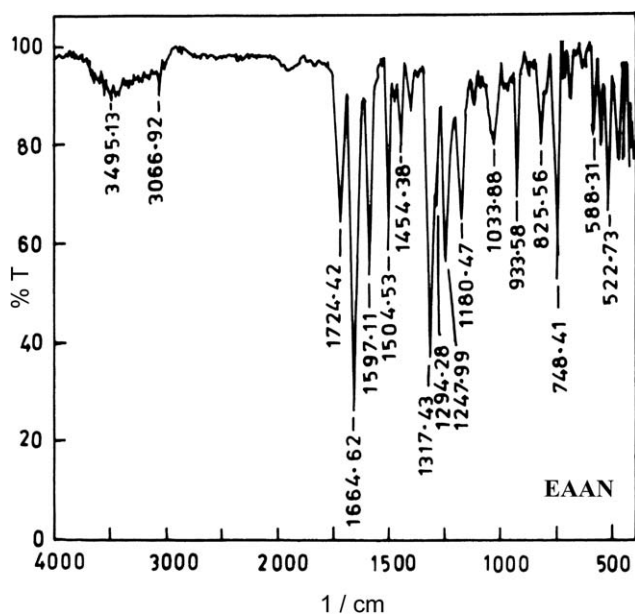


Figure 1 IR(KBr pellet) spectrum of EAAN.

mol (1.44 g) acrylic acid, and 0.5 g triethyl amine as a catalyst. The reaction mixture was refluxed with stirring for 4 h. Excess solvent was distilled off and reddish brown transparent solid resin was isolated from water, filtered, washed well water, and dried at 50°C. EAAN was purified three times from chloroform-*n*-hexane system prior to its use.

Measurements

IR(KBr pellet) and $^1\text{H-NMR}$ spectra of EAAN were scanned on a Shimadzu-8400 FTIR spectrometer over the frequency range from 4000 to 400 cm^{-1} and on a Bruker AVANCE II (400 MHz) spectrometer by using CDCl_3 as a solvent and TMS as an internal standard. The acid and hydroxyl values of EAAN were determined according to reported method.¹³ Observed acid and hydroxyl values of EAAN are 7.92 and 741.50 mg KOH/g, respectively. Molecular weights and molecular weight distribution of EAAN were determined by Perkin-Elmer GPC (series 200) using THF as a solvent and standard polystyrene mixed bed at 30°C. Observed weight average, number average molecular weights and molecular weight distribution are $\overline{M}_w = 5300$, $\overline{M}_n = 2980$, and $\overline{M}_w/\overline{M}_n = 1.79$, respectively.

The 2% solutions of EAAN were prepared in selected solvents and from them a series of dilute solutions were prepared at room temperature. The density (ρ), viscosity (η), and speed of ultrasound (U) of pure solvents and EAAN solutions were carried out at 303, 308, and 313 ± 0.1 K by using specific gravity bottle, Ubbelohde suspended level viscometer and Mittal Enterprise Interferometer (New Delhi) Model No F-81 operating at 2 MHz, respectively. The

ρ , η , and U measurements were accurate to ± 0.1 kg/ m^3 , ± 0.01 mPa s, and $\pm 0.15\%$, respectively.

RESULTS AND DISCUSSION

IR and NMR spectral characterization

Figure 1 shows IR spectrum of EAAN. Observed characteristic absorption peaks (cm^{-1}) of polymer chain and aromatic groups are as follows: 3495.1 ($-\text{OH}$ str.), 3066.92 ($-\text{CH}$ str.), 1724.42 ($\text{C}=\text{O}$ str.), 1597.1 ($\text{C}=\text{C}$ str.), and 1247.99 ($\text{C}-\text{O}-\text{C}$ str.). Figure 2 shows $^1\text{H-NMR}$ spectrum of EAAN. Different types of protons and chemical shifts (ppm) are assigned as follows: 8.215–8.197[d, $-\text{CH}$ (c)], 7.481–7.413[m, $-\text{CH}$ (e + d)], 7.158–7.130[d, $-\text{CH}$ (f)], 6.858–6.840[d, $-\text{CH}$ (b)], 6.767–6.748[d, $-\text{CH}$ (a)], 6.441–6.351[d, $=\text{CH}_2$], 6.192–6.098[m, $=\text{CH}-\text{C}=\text{O}$], 5.810–5.874[d, $=\text{CH}_2$], 4.754–4.778[t, $-\text{OCH}_2$ (epoxy chain)]. Thus, IR and NMR spectral data supported the structure of EAAN.

Molecular interaction study

Experimental data on ρ , η , and U of pure solvents and EAAN solutions at 303, 308, and 313 K are summarized in Table I from which it is observed that ρ decreased linearly with C and T in CF, while it increased linearly with C and decreased with T in DO and THF. Both η and U increased linearly with C and decreased with T in all the three systems. The observed trends in ρ , η , and U are $\text{CF} > \text{DO} > \text{THF}$, $\text{DO} > \text{CF} > \text{THF}$, and $\text{DO} > \text{THF} > \text{CF}$, respectively. The ρ , η , and U data are correlated with concentration (C) and temperature (T). The least square equations along with regression coefficients (R^2) are reported in Table II from which it is observed that a fairly good to

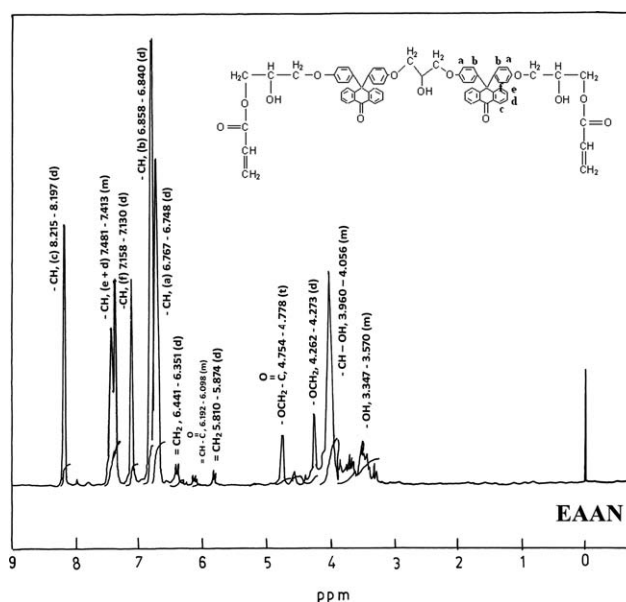


Figure 2 NMR spectrum of EAAN in CDCl_3 .

TABLE I
Density (ρ), Viscosity (η), and Speed of Ultrasound (U) Data of EAAN Solutions at 303, 308, and 313 K

Conc. (%)	Density ρ (kg/m ³)			Viscosity η (10 ³ , Pa s)			U (ms ⁻¹)		
	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
EAAN-CF									
0	1475.8	1472.7	1467.9	0.570	0.535	0.481	968	948.8	930.4
0.25	1474.5	1472.2	1467.3	0.575	0.540	0.483	965.2	949.2	931.6
0.50	1473.7	1471.6	1467	0.585	0.555	0.488	966.8	950	932.4
1	1472.8	1470.5	1466.1	0.603	0.571	0.506	967.6	950.8	933.6
1.50	1472.5	1469.5	1464.5	0.618	0.594	0.533	968.4	951.6	934.8
2.0	1471.9	1468.1	1463.7	0.660	0.619	0.544	970	952.8	936
EAAN-DO									
0	1026.3	1024.7	1021.3	1.067	0.992	0.859	1314.8	1294	1270
0.25	1026.5	1025.1	1022.4	1.087	1.000	0.880	1316	1295.6	1272
0.50	1027.6	1025.6	1023.3	1.108	1.015	0.897	1316.4	1296.4	1274
1	1028.4	1026.8	1023.7	1.136	1.065	0.928	1317.6	1296.8	1276.4
1.50	1029.6	1027.8	1024.2	1.167	1.104	0.966	1318.8	1298.4	1278.4
2.0	1030.9	1029	1025.6	1.209	1.130	1.007	1320	1299.6	1280
EAAN-THF									
0	879.1	876.4	874.1	0.466	0.432	0.385	1254.4	1232.8	1206
0.25	880.8	878.5	875.9	0.472	0.443	0.398	1256	1233.2	1208.4
0.50	881.6	879.9	876.6	0.484	0.451	0.404	1256.8	1234.4	1210
1	883.7	881.7	878	0.506	0.469	0.415	1258	1235.6	1212
1.50	885.1	883.3	880.2	0.525	0.489	0.435	1259.2	1236.4	1215.6
2.0	886.3	884.3	882.8	0.547	0.508	0.453	1261.2	1238.8	1218

excellent correlation ($R^2 = 0.921$ – 0.996) is observed. The change in ρ and U with C and T are not as appreciable as η due to molecular interactions.^{7–9,14–20}

Physical properties namely density, viscosity, refractive index, isentropic compressibility, intermolecular free length, free volume, etc. affect speed of ultrasound in different organic solvents and solutions. Because of molecular interactions the structure of the solute is modified and hence physical properties under consideration change accordingly.

The linear increase of ρ , η , and U with C confirmed increase of cohesive forces because of strong molecular interactions, while decrease of these parameters with T supported decrease of cohesive forces. The

increase in temperature has two opposite effects namely structure formation (intermolecular association) and structure destruction. The structure forming tendency is mainly due to solute–solvent interactions, while destruction of structure formed previously is due to thermal fluctuations.^{7,14} When thermal energy is greater than that of interaction energy, it causes destruction in structure formed previously.

The density, viscosity, and speed of ultrasound data are useful in determining various acoustical parameters such as specific acoustical impedance (Z), isentropic compressibility (κ_s), intermolecular free path length (L_f), classical absorption coefficient (α/f^2)_{cl}, and viscous relaxation time (τ), which

TABLE II
The Least Square Equations and Regression Coefficients for EAAN at 303, 308, and 313 K

Parameters	Least square equations (regression coefficients, R^2)		
	303 K	308 K	313 K
EAAN-CF			
ρ (kg m ⁻³)	$-1.387C + 1474$ ($R^2 = 0.938$)	$-2.290C + 1472$ ($R^2 = 0.996$)	$-2.173C + 1468$ ($R^2 = 0.983$)
η (mPa s)	$0.045C + 0.560$ ($R^2 = 0.950$)	$0.043C + 0.529$ ($R^2 = 0.993$)	$0.035C + 0.471$ ($R^2 = 0.994$)
U (ms ⁻¹)	$2.439C + 965.0$ ($R^2 = 0.952$)	$1.941C + 948.8$ ($R^2 = 0.989$)	$2.380C + 931.1$ ($R^2 = 0.921$)
EAAN-DO			
ρ (kg m ⁻³)	$2.378C + 1027$ ($R^2 = 0.987$)	$2.495C + 1024$ ($R^2 = 0.994$)	$1.604C + 1022$ ($R^2 = 0.940$)
η (mPa s)	$0.067C + 1.080$ ($R^2 = 0.994$)	$0.088C + 0.986$ ($R^2 = 0.996$)	$0.071C + 0.860$ ($R^2 = 0.996$)
U (ms ⁻¹)	$2.322C + 1315$ ($R^2 = 0.998$)	$2.224C + 1295$ ($R^2 = 0.972$)	$4.468C + 1271$ ($R^2 = 0.979$)
EAAN-THF			
ρ (kg m ⁻³)	$3.207C + 880.1$ ($R^2 = 0.988$)	$3.287C + 878.0$ ($R^2 = 0.977$)	$3.902C + 874.6$ ($R^2 = 0.981$)
η (mPa s)	$0.042C + 0.462$ ($R^2 = 0.999$)	$0.037C + 0.432$ ($R^2 = 0.999$)	$0.032C + 0.387$ ($R^2 = 0.985$)
U (ms ⁻¹)	$2.848C + 1255$ ($R^2 = 0.988$)	$2.917C + 1232$ ($R^2 = 0.966$)	$5.512C + 1207$ ($R^2 = 0.993$)

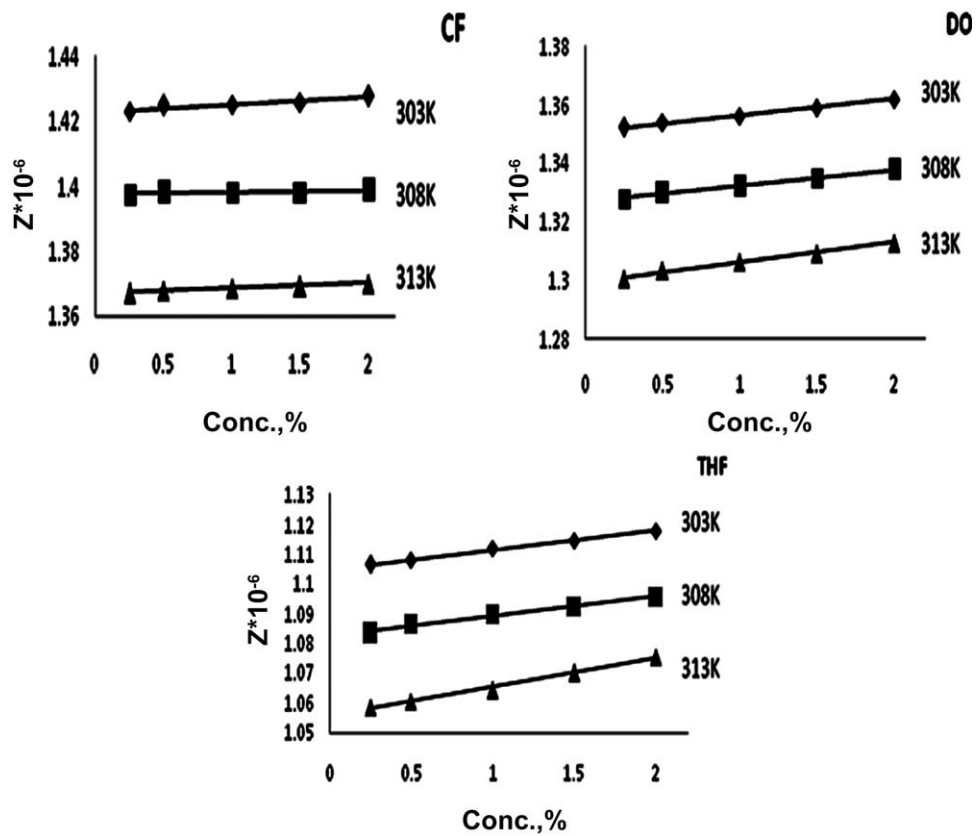


Figure 3 The plots of Z against C for EAAN solutions at 303, 308, and 313 K.

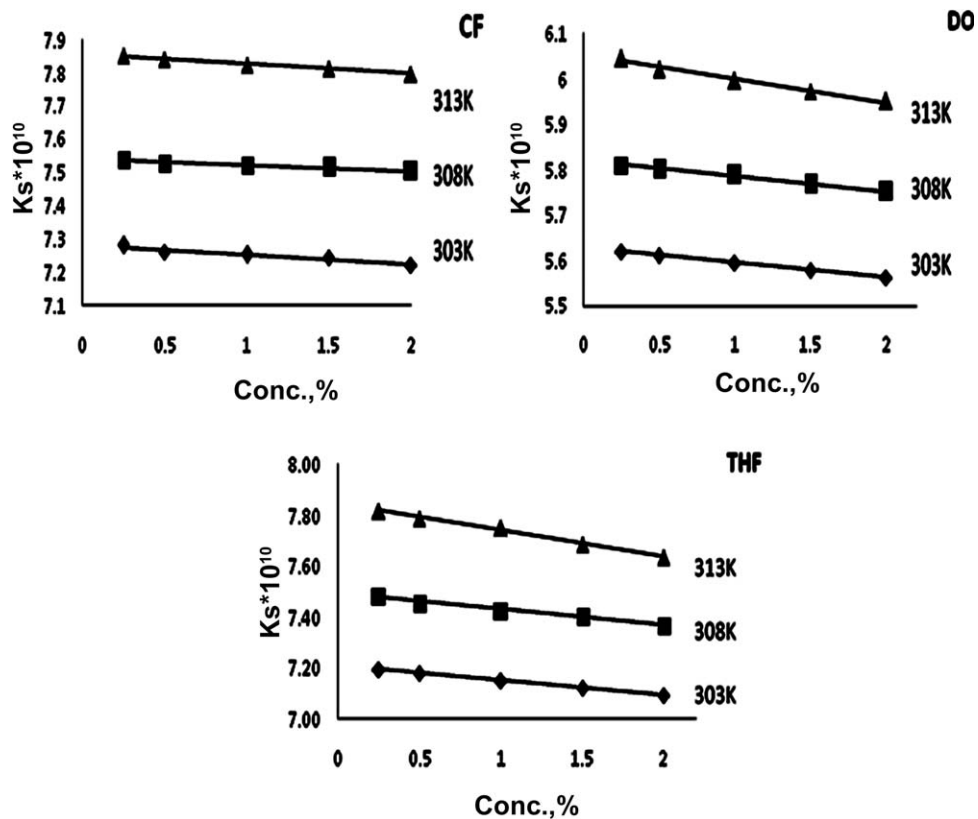


Figure 4 The plots of κ_s against C for EAAN solutions at 303, 308, and 313 K.

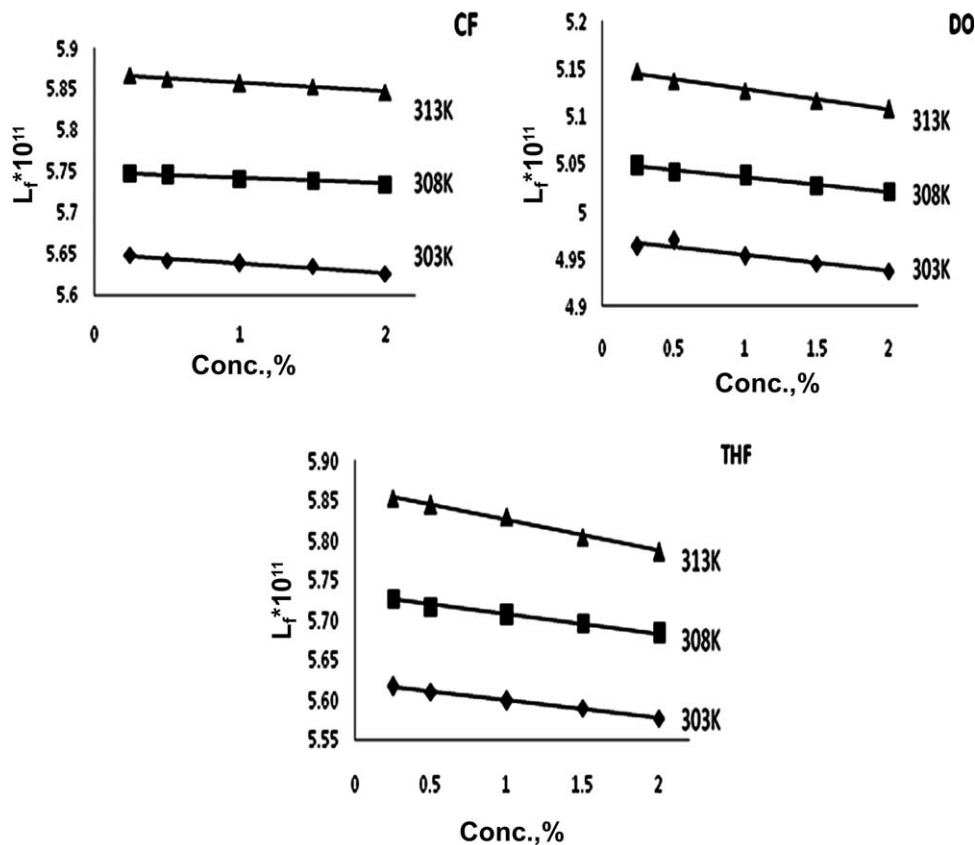


Figure 5 The plots of L_f against C for EAAN solutions at 303, 308, and 313 K.

furnish further knowledge on molecular interactions occurring in the solutions as well as useful in polymer processing technology especially from solutions.

Theoretical equations for acoustical parameters

1. Specific acoustical impedance:

$$Z = U\rho \quad (1)$$

2. Isentropic compressibility:

$$\kappa_s = \frac{1}{U^2\rho} \quad (2)$$

3. Intermolecular free path length:

$$L_f = K(\kappa_s)^{1/2} \quad (3)$$

where $K = (93.875 + 0.375T) \times 10^{-8}$ is a temperature dependent constant.

4. Classical absorption coefficient:

$$\left(\frac{\alpha}{f^2}\right)_{cl} = \frac{8\pi^2\eta}{3U^3\rho} \quad (4)$$

Classical absorption coefficient has its origin in the viscosity of the medium.

5. Viscous relaxation time.

The resistance offered by viscous force in the flow of sound wave appears as a classical absorption associated with viscous relaxation time:

$$\tau = \frac{4\eta}{3\rho U^2} \quad (5)$$

To understand the effect of concentration, temperature, nature of solvents and solute on molecular interactions in solutions, above-mentioned acoustical parameters are determined according to eqs. (1)–(5) and are correlated with C and T (Figs. 3–7). A fairly good to excellent correlation between a particular parameter and C is observed for a given temperature and solvent systems studied. The Z (regression coefficient $R^2 = 0.904$ – 0.998), τ ($R^2 = 0.993$ – 0.999), and $(\alpha/f^2)_{cl}$ ($R^2 = 0.984$ – 0.999) increased linearly with C and decreased with T , while κ_s ($R^2 = 0.945$ – 0.998), and L_f ($R^2 = 0.913$ – 0.993) both decreased linearly with C and increased with T in CF, DO, and THF. Increase or decrease of acoustical parameters with C and T indicated presence of strong molecular interactions in the solutions.

Variation of U in the solution depends on intermolecular free length. When ultrasonic waves are incident on the solution, the molecules get perturbed. Since the medium has some elasticity and hence

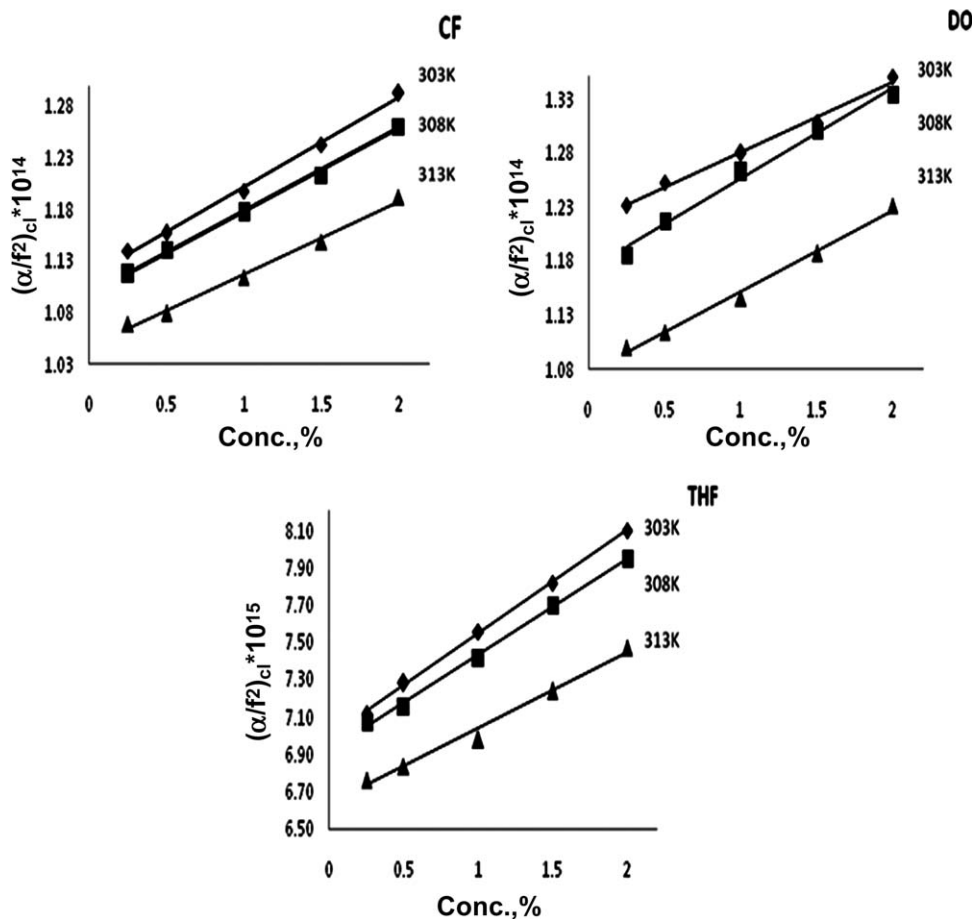


Figure 6 The plots of $(\alpha/f^2)_{cl}$ against C for EAAN solutions at 303, 308, and 313 K.

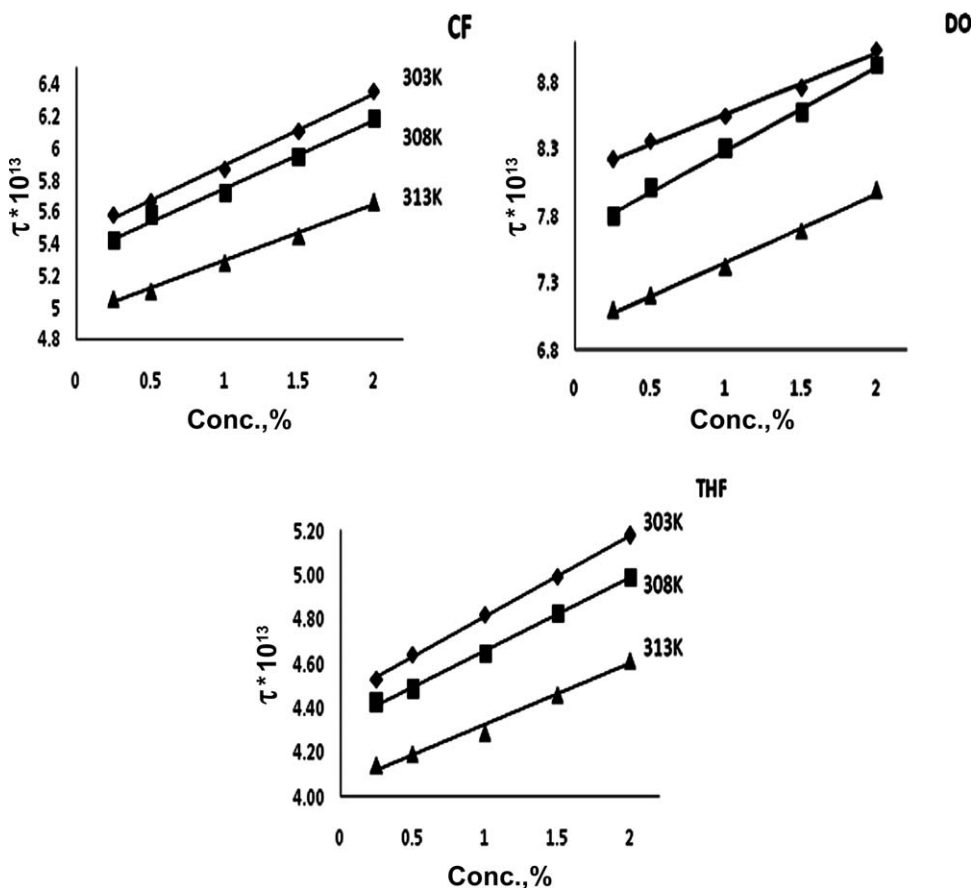


Figure 7 The plots of τ against C for EAAN solutions at 303, 308, and 313 K.

perturbed molecules regain their equilibrium positions. When a solute is added to a solvent, its molecules attract certain solvent molecules towards them. The phenomenon is known as compression and also as limiting compressibility. Generally κ_s and L_f decrease with C . The aggregation of solvent molecules around solute molecules supports strong solvent–solute interactions and hence considerable change in structural arrangement. Relaxation process causes dispersion of U in the system. Molecular interactions such as solvent–solute interactions, quantum mechanical dispersive forces, and dielectric force may cause either contraction or expansion and hence change in transport properties of the solutions.

The ester, ether, carbonyl, and hydroxyl groups of EAAN are polar groups, which are responsible for structure formation with solvents, i.e., molecular association. It is likely that OH groups of EAAN form H-bonds with Cl atoms of CF and lone pairs of electrons of THF and DO, while ester and carbonyl groups form H-bonds with H atom of CF. Molecular association affects both apparent molar volume as well as molecular weight and as a consequence ρ , η , and U vary with C and T . Linear increase or decrease of the acoustical parameters with C confirmed predominant solvent–solute interactions over solute–solute interactions and dispersion forces.

CONCLUSION

1. Density (except CF system), viscosity, and speed of ultrasound increased with concentration and decreased with temperature confirming change in cohesive forces due to strong molecular interactions.
2. The presence of strong molecular interactions is further supported by various acoustical parameters.
3. EAAN has structure forming tendency.

4. Knowledge of molecular interactions in resin solutions is very useful in processing technology especially change in dimensions, associated solvents, etc.

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