STRUCTURAL INTERACTION OF NOVEL DENDRIMER AND SUBUNITS WITH WATER ESTIMATED WITH EXCESS MOLAR VOLUMES, VISCOSITIES AND FREE ENERGIES

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ABSTRACT. The 2,4,6-tridiethylmalonatetriazine (TDEMTA) dendrimer and subunits developed interaction potential when mixed with water due to structural reorientation. Thus excess volumes ($V^E 10^{-6}$ m^3 mol^{-1}), viscosities ($\eta^E/0.1$ N s m^{-2}) and molar free activation energy (ΔG^E kJ mol^{-1} K^{-1}) from 0.63 to 10 mm kg^{-1} of 2,4,6-trichlorotriazine (TCT), 2,4,6-triacetotriazine (TAT), 2,4,6-trihydroxytriazine (THT) and 2,4,6-tridiethyl-malonatetriazine (TDEMTA) have been reported with water at 298.15 K. The V^E and η^E positive values inferred deviations from ideal behavior with an adequate potential to cause solute-solvent interactions. The ideally the $V^E = 0$ and $\eta^E = 0$, and their η^{E0} noted as limiting excess viscosities were as TAT > 2,4,6-trihydroxytriazine (THT) = 2,4,6-trichlorotriazine (TCT) > 2,4,6-tridiethylmalonatetriazine (TDEMTA). The $\Delta G^E > 0$, was higher by 15.15 kJ mol^{-1} K^{-1} with weaker interacting response of the dendrimer. The 3 x 10^{-4} mm kg^{-1} 2,4,6-trihydroxytriazine (THT) showed higher ΔG^E values with an abrupt decrease with much disruption in molecular interaction similar to surfactant behavior. The lowest ΔG^E values were with the 2,4,6-trichlorotriazine (TCT) due to comparatively higher interactions of the chloride ion.

KEY WORDS: Excess viscosity, Trichlorotriazine, Hydrophilic, Hydrophobic, Hydrodynamic

INTRODUCTION

Structural interacting potential of the dendrimers is of industrial significance [1-2] for wider reorientations and binding affinities with energy consumption [3]. In general, the dendrimers are used in drug designing and transporting, molecular binding, ionic trapping only due to non-reacting but highly interacting potential and interacting molecular activities. The physicochemical indicators most effectively decide interacting capacity of any new molecule and hence the physicochemical data of the 2,4,6-tridiethylmalonatetriazine (TDEMTA) are studied. The 2,4,6-tridiethylmalonatetriazine (TDEMTA) is newly prepared dendrimer molecule, its preparation and characterization are reported elsewhere [4]. Special molecular structures of dendrimers do develop two types of interactions as their triazine and branching both have different electronic configurations and electronic densities. This led to disrupt hydrogen bonded water with utilization of free energies. The dendrimers are reported as anticancer and drug carriers because both of the core and branching contribute to bind the foreign moieties. There are enough void spaces between core and branching. So solvation and interaction study with solvents are essential [4-6] and several subunits are used for dendrimer preparation where solubility and interacting nature do decide fate of their mixtures. Thus, the physical data on reaction engineering are guiding factors [7-11] to decide and widen their applications. The densities, viscosities and energy render an effective assistance for successful manufacturing of new materials and their interacting nature. Our data on aqueous mixtures of the 2,4,6-trichlorotriazine (TCT), 2,4,6-triacetotriazine (TAT), 2,4,6-trihydroxytriazine (THT) and 2,4,6-tridiethylmalonatetriazine (TDEMTA) [1] assessed reactivity and interaction [12] profile whose preparation and characterization are reported in earlier work [4].

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EXPERIMENTAL

Both the 2,4,6-trichlorotriazine (TCT) (AR, E Merck, India) and sodium diethylmalonate (AR, E Merck, India), were used as received and the 2,4,6-triacetotriazine (TAT), 2,4,6-trihydroxytriazine (THT) and 2,4,6-tridiethylmalonatetriazine (TDEMTA) were prepared and reported in previous paper [4]. The molecules were purified and characterized by standard laboratory methods [15-17]. The 2,4,6-tridiethylmalonatetriazine (TDEMTA) was prepared by using sodium diethylmalonate [$NaCH(COOC_2H_5)_2$, a sodium salt of malonate ester (SDEM) [4]. The aqueous 2,4,6-trichlorotriazine (TCT), 2,4,6-triacetotriazine (TAT), 2,4,6-trihydroxytriazine (THT) and 2,4,6-tridiethylmalonatetriazine (TDEMTA) mixtures were prepared for study. Their molecular structures are depicted in Figure 1.

2,4,6-Tridiethylmalonatetriazine (TDEMTA)   2,4,6-Trichlorotriazine (TCT)

2,4,6-Triacetotriazine (TAT)   2,4,6-Trihydroxytriazine (THT)
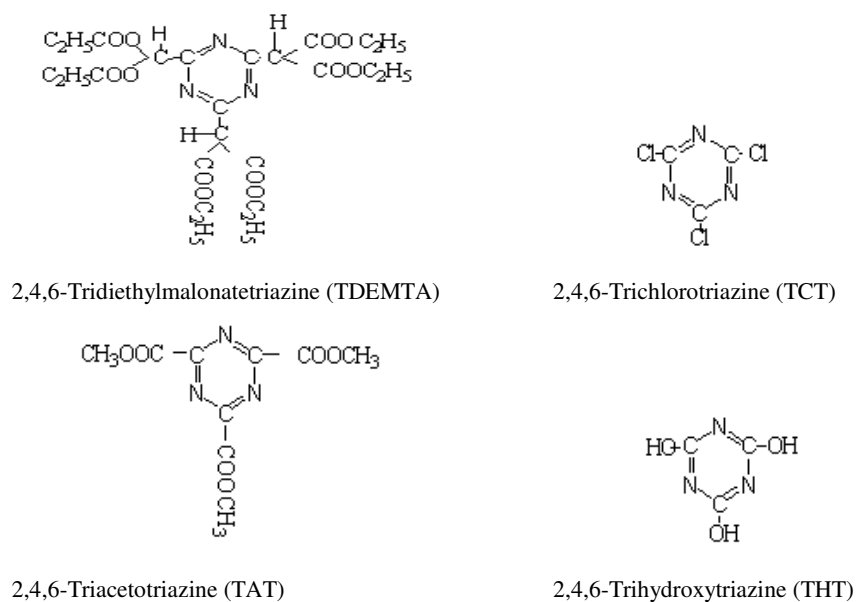
Figure 1. The molecular formula of 2,4,6-trichlorotriazine (TCT), 2,4,6-triacetotriazine (TAT), 2,4,6-trihydroxytriazine (THT) and 2,4,6-tridiethylmalonatetriazine (TDEMTA).

The above strctures do illustrate the interacting constituents of the molecules which help in design the operational molecular models. The densities were measured with 20×10^{-3} dm^3 bicapillary pyknometer of 14.76643 g, and flow times with Survismeter at 298.15 and 303.15 K with ± 0.01 ^0C control, noted with Beckman thermometer. The Survismeter was procured from Borosil India. The flow times were noted with an electronic timer ± 0.01 s and the weights were obtained with 0.01 mg accuracy analytical Dhona balance model 100 DS (Instrumentation Pvt. Ltd. Calcutta, India) for densities. The Survismeter was mounted in 20 L capacity water bath of thermostat [14, 15].

Calculations

The densities ρ were calculated with weights by equation 1:

$$\rho = [((w-w_0)/(w_0-w_e))\rho_0 + 0.0012(1-(w-w_0/w_0-w_e))] \tag{1}$$

The ρ_0 is density of solvent, and $0.0012(1-(w-w_0/w_0-w_e)$, a buoyancy correction for air in weights, the w_e, w_0 and w denote the weights of empty, solvent and solution filled pyknometer, respectively. The viscosities (η) were calculated by equation 2:

$$\eta = ((\rho.t)/(\rho_0.t_0))\eta_0 \tag{2}$$

The t and t_0 are flow times for solution and solvent, and η and η_0 the viscosities, respectively. The V_2 values were computed from the ρ data by equation 3:

$$V_2 = 1/\rho((M-(1000/m)((\rho-\rho_0)/(\rho_0)) \tag{3}$$

The M is molar mass. Uncertainties in the V_2 data were calculated by equation 4:

$$V_2 = \pm (1000/m)\Delta\rho/\rho \tag{4}$$

The $\Delta\rho = \rho - \rho_0$. The excess viscosities η^E were calculated by equation 5:

$$\eta^E = \eta - \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2) \tag{5}$$

The x_1, x_2 and η_1, η_2 are mole fractions and viscosities of solvent and molecules, respectively. Excess volumes V_2^E are calculated by equation 6:

$$V_2^E = [x_1M_1 + x_2M_2/\rho]-[x_1V_1 + x_2V_2] \tag{6}$$

The V_1 is apparent molal volume of the water and the V_2 of the molecules in mixtures, the M_1 and M_2 respective molar masses. Excess molar free activation energy ΔG^E were calculated by equation 7:

$$\Delta G^E = RT [\ln \eta_2 V_2 - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2)] \tag{7}$$

RESULTS AND DISCUSSION

The excess data are reported in Table 1 and excess viscosities are plotted in Figure 2 where the 2,4,6-tridiethylmalonatetriazine (TDEMTA) is noted with lowest limiting excess viscosities. The lower values inferred weaker binding of solvent with the 2,4,6-tridiethylmalonatetriazine with comparatively weaker entanglement of the water molecules during viscous flow.

Excess viscosity η^E

The η^E data depict deviation from an ideal behavior due to interactions where the positive deviations in values inferred stronger and the negative deviations weaker interactions. The 2,4,6-triacetotriazine (TAT) > 2,4,6-trihydroxytriazine (THT) = 2,4,6-trichlorotriazine (TCT) > 2,4,6-tridiethylmalonatetriazine (TDEMTA) trend did infer stronger solvent entanglement that slowed down the viscous flow with higher excess limiting viscosities of the 2,4,6-triacetotriazine (TAT) (Figure 2). The molecules showed positive η^E values that denote activities like solubilization, hydration and functionality of attached groups. In general, the ideal mixture does not interact and no variations in data of the parameters are noted. For example benzene and water on mixing do not show any change in respective data because they do not interact. Thus excess data do infer interaction in the mixtures. The excess viscosity for 2,4,6-trichlorotriazine (TCT), 2,4,6-triacetotriazine (TAT), and 2,4,6-trihydroxytriazine (THT) are slightly higher as compared to 2,4,6-tridiethylmalonatetriazine (TDEMTA) with a negligible increment with increase in mole fractions. As their solutions remained near Newtonian ones, with a constant rate of viscosity increment with similar shear on laminar flow. Probably with composition increase the molecules keep interacting with the water molecules without formation of any

peculiar structure like micelles, etc. Hence more and more water molecule keep interacting with dendrimers. The slope values are considerably low and depicted along equations written in Figure 2, the values are almost the same which inferred that their composition effect are almost the same. The excess viscosities η^E (Table 1) increased from 2 x 10^{-4} millimole fractions (mmf) with maximum values at higher mole fractions. This slight increase in the η^E values depicted a disruption of the hydrogen bonding of the water. The positive η^E values for 2 x 10^{-4} to 1.5 x 10^{-3} mmf inferred a complex formation due to pair wise interaction complex.

Table 1. Densities, $\rho/10^3$ kg m^{-3}, viscosities, $\eta/0.1$ N s m^{-2}, excess viscosities, $\eta^E/10^{-3}$ N s m^{-2}, excess volume, $V^E 10^{-6}$ m^3 mol^{-1}, and excess free energy ΔG^E kJ mol^{-1} K^{-1}.

c, millimol kg^{-1}	ρ	η	V^E	η^E	ΔG^E
2,4,6 TDEMTA					
0.63	0.9915	0.7949	0.155	1.592	15.15
1.25	0.9915	0.7958	0.155	1.593	15.15
2.50	0.9917	0.7970	0.151	1.594	15.15
5.00	0.9918	0.7983	0.149	1.596	15.15
10.00	0.9920	0.7997	0.146	1.597	15.15
2,4,6 TCT					
0.24	2.4049	0.7994	0.155	1.597	14.77
0.18	1.8686	0.8001	0.154	1.597	14.77
0.14	1.4968	0.8012	0.154	1.598	14.77
0.08	0.8303	0.8015	0.153	1.599	14.77
0.10	0.9916	0.8018	0.153	1.599	14.77
2,4,6 TAT					
0.63	0.9913	0.8006	0.158	1.598	15.15
1.25	0.9913	0.8032	0.158	1.600	15.15
2.50	0.9915	0.8047	0.154	1.602	15.15
5.00	0.9917	0.8062	0.150	1.603	15.15
10.00	0.9918	0.8085	0.149	1.606	15.15
2,4,6 THT					
0.63	0.9915	0.8005	0.155	1.598	15.16
1.25	0.9915	0.8018	0.154	1.599	15.16
2.50	0.9916	0.8026	0.154	1.600	15.16
5.00	0.9969	0.8070	0.567	1.604	15.14
10.00	0.9973	0.8082	0.485	1.605	15.14

The molecules showed a poor solubility and hence the study of the η^E was made at lower mole fraction. The 2,4,6-trichlorotriazine (TCT) showed a slightly higher increase in viscosities for 2 x 10^{-4} mmf and onwards with comparatively higher shear approaching towards Non-Newtonian fluids. It is termed as plastic fluid with a pseudoplastic point at around 2 x 10^{-4} and 2.5 x 10^{-4} mmf for 2,4,6-trihydroxytriazine (THT) and 2,4,6-trichlorotriazine (TCT) respectively with a Non-Newtonian behavior. However the 2,4,6-trihydroxytriazine (THT) and 2,4,6-trichlorotriazine (TCT) as pseudoplastic materials, in general, decrease viscosities but the decrease at 273.15 K or below is lower in comparison to 303.15 K. The two factors are responsible for such behavior (a) due to interacting molecular activities (b) the increase in temperature. As the higher temperature further weakens intermolecular forces that decrease the viscosities due to comparatively higher flow rates. The pseudoplastic point showed a variation in shear strength. So except 2,4,6-trichlorotriazine (TCT) and 2,4,6-trihydroxytriazine (THT), the other molecules developed thixotropic solutions and 2,4,6-trichlorotriazine (TCT) and 2,4,6-trihydroxytriazine (THT) the rheotropic which does cause stronger interaction with higher shear rate. The 2,4,6-trichlorotriazine (TCT) with 3 chloride atoms, attached at 160^0 to each other,

held water molecules in void spaces in its electronic zone which is very useful for developing drug delivery systems and to transfer drug from one side to another. The 2,4,6-triacetotriazine (TAT) showed the maximum η^E values with an effective hydrodynamic structure and water entered in void spaces in its electronic zone caused certain restriction on its rotational, transnational and kinetic motions. The 2,4,6-tridiethylmalonatetriazine (TDEMTA) with lower η^E values showed weaker response to a hydrodynamic model because in a void space of a dendrimer-water complex, the 6 ethyl units occupied the maximum area around the triazine ring. This inferred a water binding capacity of triazine core due to 3 N atoms in its ring 2,4,6-trichlorotriazine (TCT) and others. The lower hydrodynamic volume of the 2,4,6-tridiethyl-malonatetriazine (TDEMTA) is because comparatively less water molecules are get chance to bind with triazine as the 6 ethyl units are attached. The 2,4,6-trihydroxytriazine (THT) with 3-OH groups showed higher η^E values than those of the 2,4,6-tridiethylmalonatetriazine (TDEMTA) and lower than of the TAT due to development of slightly stronger hydrogen bonding of the -OH groups with hydrophilic interactions as compared to other molecules. This also distinguished a development of the hydrophobic interactions of the 2,4,6-tridiethyl-malonatetriazine (TDEMTA) with 6 ethyl units than of the hydrophilic of the THT with -OH groups.

The densities are as 2,4,6-trihydroxytriazine (THT) = 2,4,6-trichlorotriazine (TCT) > 2,4,6-tridiethylmalonatetriazine (TDEMTA) > 2,4,6-triacetotriazine (TAT) at 0.63 and 1.25 mm kg^{-1}, 2,4,6-tridiethylmalonatetriazine (TDEMTA) > 2,4,6-trihydroxytriazine (THT) = 2,4,6-trichloro-triazine (TCT) > 2,4,6-triacetotriazine (TAT) at 2.5 mm kg^{-1} and 2,4,6-trihydroxytriazine (THT) > 2,4,6-tridiethylmalonatetriazine (TDEMTA) > 2,4,6-triacetotriazine (TAT) > 2,4,6-trichloro-triazine (TCT) at 5and 10 mm kg^{-1}. The viscosities are as 2,4,6-triacetotriazine (TAT) > 2,4,6-trihydroxytriazine (THT) > TCT > 2,4,6-tridiethylmalonatetriazine (TDEMTA) at 0.63, 1.25, 2.50 and 10 mm kg^{-1} and 2,4,6-trihydroxytriazine (THT) > 2,4,6-triacetotriazine (TAT) > 2,4,6-trichlorotriazine (TCT) > 2,4,6-tridiethylmalonatetriazine (TDEMTA) at 5 mm kg^{-1}. The ρ and η data illustrated weaker van der Waals forces on the 2,4,6-triacetotriazine (TAT) molecule at lower compositions (Table 1) but 2,4,6-tridiethylmalonatetriazine (TDEMTA) with 6 ethyl group weakened such forces with weaker molecular activities. The -OH and chloro increased the activities of a triazine core of the 2,4,6-tridiethylmalonatetriazine (TDEMTA). With increase in concentrations the THT exhibited the stronger van der Waals forces and a stronger structure breaker. The 2,4,6-trichlorotriazine (TCT) showed weaker forces due to Cl$^-$ but at higher concentrations the weaker van der Waals forces restricted the structure breaking action. Thus the parameters illustrated a molecular behavior of the dendrimer forming molecules for a pre-characterization.

Molar activation energy ΔG^E

The $\Delta G^E > 0$ values are (Table 1) as 2,4,6-trihydroxytriazine (THT) > 2,4,6-triacetotriazine (TAT) > 2,4,6-tridiethylmalonatetriazine (TDEMTA) > 2,4,6-trichlorotriazine (TCT) with a slight decrease from 15.15 to 14.77 kJ mol^{-1} K^{-1}. The higher ΔG^E values inferred a weaker interaction utilizing smaller amount of energy. While the 2,4,6-trichlorotriazine (TCT) showed lowest ΔG^E with maximum spontaneity with water, as the electron density of chloride atom favor the action. The ΔG^E values for 2,4,6-tridiethylmalonatetriazine (TDEMTA), 2,4,6-trichlorotriazine (TCT) and 2,4,6-triacetotriazine (TAT) showed a slight increment by 0.02 J mol^{-1} K^{-1} but for the 2,4,6-trihydroxytriazine (THT) the ΔG^E values are higher than those of others at 4 x 10^{-4} mmf with a sharp decrease up to 6x10^{-4} mmf and further increase slightly from 6.5 x 10^{-4} to 1.4 x 10^{-3} mmf with a possibility of micelle formation. At this concentration the larger molecules of 2,4,6-trihydroxytriazine (THT) with three -OH groups forming hydrogen bond get accumulated. A sharp decrease in ΔG^E values denotes a higher solubility of the 2,4,6-

trihydroxytriazine (THT), with development of stronger hydrogen bonds with water. The $\Delta G^E >$ 0 values inferred a dominance of the hydrophobicity with weaker solubility. The slightly lower ΔG^E values with 2,4,6-tridiethylmalonatetriazine (TDEMTA) denoted comparatively stronger reorientation in solvent molecules. The positive ΔG^E values showed an optimization in interactions. Thus the water molecules formed a cage around a hydrophobic part except 2,4,6-trihydroxytriazine (THT), with slightly smaller ΔG^E consumption for 2,4,6-tridiethyl-malonatetriazine (TDEMTA). It inferred inability to break the water structure. So the water is not a good solvent for solubilization as the 6 sites of 2,4,6-tridiethylmalonatetriazine (TDEMTA) are blocked with ethyl groups, which restricted interaction.
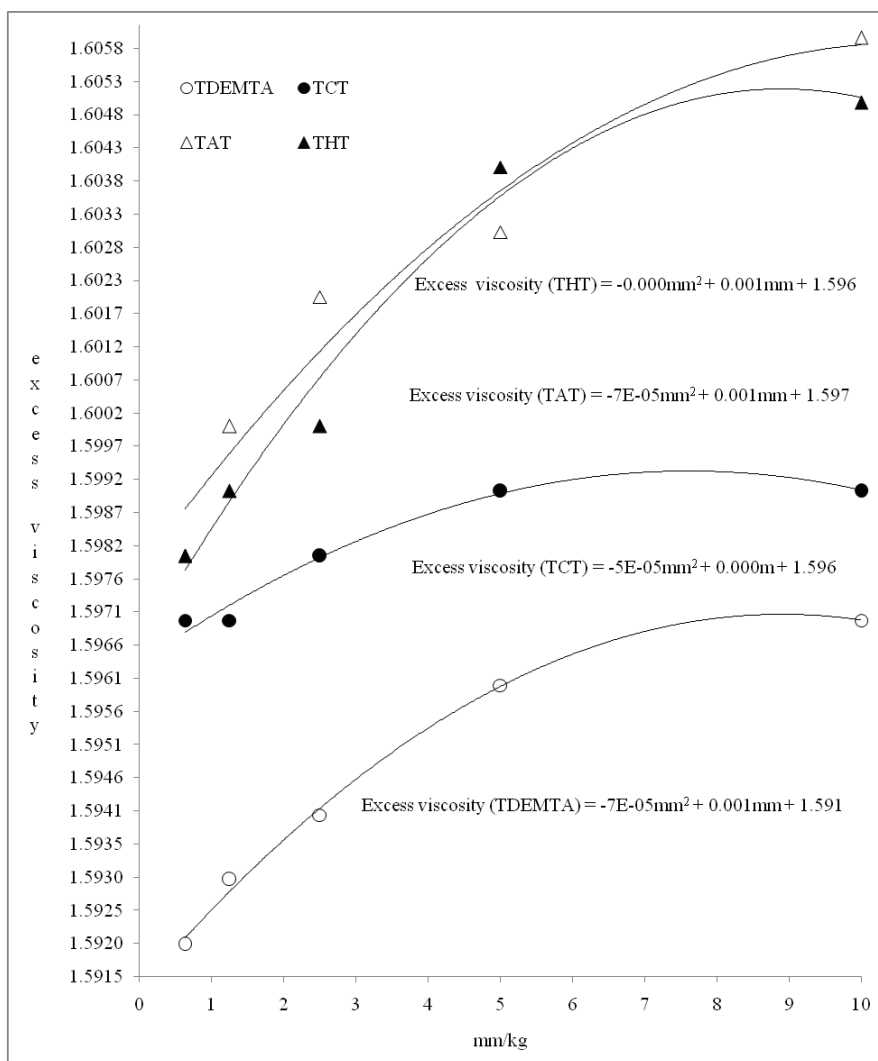

Figure 2. Excess viscosity of molecules with slopes noted along the plots.

Excess volume V^E

The $V_2^E > 0$ values as 2,4,6-trihydroxytriazine (THT) > 2,4,6-triacetotriazine (TAT) > 2,4,6-trichlorotriazine (TCT) > 2,4,6-tridiethylmalonatetriazine (TDEMTA) having values from 0.048 to 0.158 x 10^{-6} m^3 mol^{-1} range. The V_2^E values are attributed to an electrostatic structure where the lower values depict a dominance of hydrophobic and weakening of hydrophilic interactions. The V_2^E values (Table 1) of the THT increased from 0.75 x 10^{-4} to 4 x 10^{-4} mmf, and also decreased up to 9 x 10^{-4} mmf due to weaker heteromolecular forces, and -OH group caused an effective electrostatic pressure on tri-azine ring. The interacting molecular forces which are developed among mixtures of two different molecules are noted as heteromolecular forces. In context of rise in temperature, the heteromolecular forces are weakened because the thermal energy act as destructive forces among two different molecules present in mixture. Thus the weaker molecular realignments take place at 303.15 K as compared to 273.15 K or below due to molecular force theory and diversified molecular force theory. Thus the 2,4,6-trihydroxytriazine (THT)-2,4,6-trihydroxytriazine (THT) interactions with increase in concentration weakened the electrostatic forces of the 2,4,6-trihydroxytriazine (THT) and water. Also from 4 x 10^{-4} to 1.4 x 10^{-3} mmf an increase in the V_2^E values inferred stronger intermolecular forces. The similar order of the V^E values with 2,4,6-triacetotriazine (TAT) was noted while the V_2^E values with 2,4,6-tridiethylmalonatetriazine (TDEMTA) continuously decreased with increase in mole fractions. The 3 nitrogen atoms in the triazine ring and 12 oxygen atoms in side chains of the 2,4,6-tridiethylmalonatetriazine developed weaker pair wise interaction due to their electro-negativities. This enhanced a polarity of the solution with development of the stronger 2,4,6-tridiethylmalonatetriazine (TDEMTA)-2,4,6-tridiethylmalonatetriazine (TDEMTA) interactions. The 2,4,6-trichlorotriazine (TCT) produced almost similar V_2^E values with mole fractions. It inferred that the 3 chloride atoms of the 2,4,6-trichlorotriazine (TCT) did not have stronger dipole moment so a slightly weaker interaction as compared to others is observed.

CONCLUSIONS

The V_2^E values predict a reactivity of the 2,4,6-trichlorotriazine (TCT), 2,4,6-triacetotriazine (TAT), 2,4,6-trihydroxytriazine (THT), 2,4,6-tridiethylmalonatetriazine (TDEMTA) molecules. The study focused binding mechanism, potentiality to be used as legend, with resin to develop heat resistant, thermoplastic material. The molecules are hydrophobic. Since the 2,4,6-tridiethylmalonatetriazine (TDEMTA) is a supramolecule with several molecular constituents operational in mixture and hence intramolecular multiple force theory (IMMFT) could be proposed to elucidate role core with its constituents and the branching with its constituents. Friccohesity that caters IMMFT could configure and elucidate interacting molecular forces and their diversification for optimizational state with definite entropic changes [18]. The study to exactly elaborate a structural of the IMMFT, the SEM, TEM, FTIR and C^{13}NMR, ESR and LCMS are being pursued in the lab.

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