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## Spontaneity of reactions of triazine dendric molecules in aqueous medium illustrated with excess viscosities, volumes and free energies

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The far-reaching applications of the dendric units – 2,4,6 trichloro-triazine (2,4,6 TCT), triaceto-triazine (2,4,6 TAT), trihydroxy-triazine (2,4,6 THT) and tridiethylmalonate-triazine (2,4,6 TDEMTA) for reactions in an aqueous medium have been assessed in the present study. Some of their fundamental properties, such as density and viscosity, have been measured to calculate the excess volume ( $V^E$ ), viscosity ( $\eta^E$ ) and molar free activation energy ( $\Delta G^E$ ) at 298.15 K for  $6.25\text{--}10.0 \times 10^{-4} \text{ mol kg}^{-1}$ . The positive values of  $\Delta G^E$  for such units suggest their weaker response with water. THT around  $3.0 \times 10^{-7}$  mole fraction shows maximum  $\Delta G^E$  values. The lowest values of  $\Delta G^E$  are recorded for TCT.

**Keywords:** Excess viscosity; 2,4,6 trichloro-triazine; Hydrophilic and hydrophobic interaction; Hydrodynamic viscous flow; Thixotropic; Rheopectic

### 1. Introduction

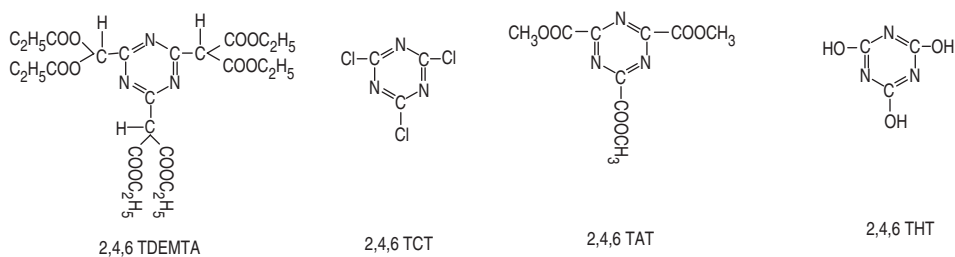
The synthesis [1,2], characterization and feasibility of the applications of some new chemical molecules have been emphasized in research [3]; and thereby, the spontaneity of such materials towards the solvation and reactivity in and with the solvents has become an additional quality of them to widen their applications [4–6] in several liquid- and solid-state processes. Pre-characterization [2,4] of the raw materials is required to determine their feasibility, reaction engineering and experimental conditions of the reaction mechanism. Therefore, physicochemical [7,8] parameters such as the densities, viscosities and energy functions provide a useful information to successfully manufacture new materials. This study contains data for the quantities mentioned above for the binary systems of 2,4,6 trichloro-triazine (2,4,6 TCT), 2,4,6 triaceto-triazine (2,4,6 TAT), 2,4,6 trihydroxy-triazine (2,4,6 THT), and 2,4,6 tridiethylmalonate-triazine (2,4,6 TDEMTA) dendric [9–11] molecules in aqueous solutions. Additionally, the data illustrate the industrial aspect of their spontaneity of the processes and interaction [12].

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## 2. Experimental

The compounds 2,4,6 TCT (AR), sodium hydroxide (AR), acetic acid (AR), diethylmalonate (AR) were procured from Merck, and the 2,4,6 TCT were dried in oven at 110°C for 24 h, and stored in P<sub>2</sub>O<sub>5</sub> vacuum desiccators. The 2,4,6 TAT, 2,4,6 THT and 2,4,6 TDEMTA were prepared by substituting [13] the Cl<sup>-</sup> atoms of 2,4,6 TCT by CH<sub>3</sub>COONa, NaOH and [NaCH(COOC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> sodium diethylmalonate (SDEM)], respectively. The SDEM was prepared by reacting sodium metal with diethyl malonate in alcoholic medium at NTP, taking 3.6 g sodium metal with 50 mL ethanol followed by the addition of 20.65 mL of diethylmalonate. The reaction started instantaneously forming a yellowish semisolid substance with the liberation of heat, its hydrogen atom being easily replaced by sodium metal forming a yellowish amorphous and hygroscopic powder of the sodium salt of malonate ester, i.e. SDEM. The aqueous solutions of TCT and SDEM were prepared separately followed by subsequent mixing of both the solutions resulting in the formation of 2,4,6 TDEMTA.

Similarly, THT and TAT were prepared by reacting the 2,4,6 TCT and aqueous solution of sodium hydroxide and sodium acetate respectively. All the prepared materials were purified and characterized by standard laboratory methods [15–17]. The structures of the chosen compounds are illustrated below:



The densities were measured with a  $20 \times 10^{-3} \text{ dm}^3$  bicapillary pycnometer of 14.76643 g, and flow times with a Survimeter [14] at 298.15 and 303.15 K temperature with  $\pm 0.01^\circ\text{C}$  control, read with Beckman thermometer calibrated at National Physical Laboratory, New Delhi, India. The efflux times were measured with a digital electronic racer with  $1.0 \times 10^{-2} \text{ s}$  accuracy. The pycnometer weights, after drying, were obtained with a 0.01 mg accuracy analytical Dhona balance model 100DS (Inst. Pvt Ltd India) for estimation of densities. The Survimeter was mounted on a stainless steel stand kept for 30 min in a water-filled thermostat bath.

## 3. Theoretical

The densities  $\rho$  were calculated from the weights using the relation  $\rho = (w - w_0 / w_0 - w_e) \rho_0 + 0.0012(1 - (w - w_0 / w_0 - w_e))$ . Here,  $\rho$  and  $\rho_0$  denote the values of the densities of solution and solvent, respectively, and  $0.0012(1 - (w - w_0 / w_0 - w_e))$  is the buoyancy correction for air in weights, the  $w_e$ ,  $w_0$  and  $w$  are weights of the empty, solvent- and solution-filled pycnometer respectively. The viscosities ( $\eta$ ) were calculated using the equation  $\eta = (\rho t / \rho_0 t_0) \eta_0$  where  $t$  and  $t_0$  denote the flow times, and  $\eta$  and  $\eta_0$  are the viscosities for solution and water as solvent, respectively.

The  $V_\phi$  values were computed from the  $\rho$  data with,  $V_\phi = 1/\rho(M - (1000/m))(\rho - \rho_0/\rho_0)$ , where  $M$  is molar mass of the dendric unit and the uncertain with  $V_\phi = \pm(1000/m)\Delta\rho/\rho$  relation.

The excess viscosities  $\eta^E$  data were calculated using the equation

$$\eta^E = \eta - \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2) \quad (1)$$

The  $x_1$ ,  $x_2$  and  $\eta_1$ ,  $\eta_2$  are the mole fractions and viscosities of the solvent and the dendric units, respectively. The excess volumes  $V^E$  are calculated using the equation

$$V^E = [x_1 M_1 + x_2 M_2 / \rho] - [x_1 V_{\phi 1} + x_2 V_{\phi 2}] \quad (2)$$

The parameter  $V_{\phi 1}$  denotes the apparent molar volume of the solvent water and the  $V_{\phi 2}$  of the dendric unit in water, and the  $M_1$  and  $M_2$  are the molar masses.

Similarly, the excess molar free activation energy  $\Delta G^E$  are calculated as

$$\Delta G^E = RT[\ln \eta_2 V_{\phi 2} - (x_1 \ln \eta_1 V_{\phi 1} + x_2 \ln \eta_2 V_{\phi 2})] \quad (3)$$

## 4. Results and discussion

### 4.1. The excess viscosity $\eta^E$

The  $\eta^E$  values for our dendric units could illustrate their mechanism pattern in aqueous solutions, mobility, association, dissociation, homo-molecular activity along with solubilization, hydration and in the functionality of the attached groups. The excess viscosity for TCT, TAT and THT are found to be slightly higher when compared to TDEMTA with a negligible increment in mole fractions. This depicts their solutions as Newtonian solutions, which are very useful to prepare the solutions of constant viscosity. The excess viscosities  $\eta^E$  values given in table 1 have an increase from  $2.0 \times 10^{-7}$  mole fractions with shifting the maxima towards the higher mole fraction and a slight increase in the values depicts the hydrogen bond breaking action of these three compounds. The positive  $\eta^E$  values after  $2.0 \times 10^{-7}$ – $1.5 \times 10^{-6}$  mole fractions further support the trend as the homomolecular interactions start forming with complex formation of the pairwise interaction complex with water (figure 1a).

The poor solubility of these compounds in water restricts the study of  $\eta^E$  at lower mole fractions of these compounds, but the TCT shows a moderate increase in the viscosities after  $2.0 \times 10^{-7}$  mole fractions. It may be inferred that a shear is generated, so that it approaches a non-Newtonian fluid, namely a plastic fluid, having a pseudoplastic point at around  $2.0 \times 10^{-7}$  and  $2.5 \times 10^{-7}$  mole fractions for THT and TCT, respectively. Hence it can be concluded that except for TCT and THT, the other units make thixotropic solutions, while TCT and THT make rheotropic ones. The compound TCT with three chloride groups attached at  $160^\circ$  can hold water molecules in its electronic zone. This may be very useful for drug delivery systems and transfer drug from one side to another. The TAT shows maximum  $\eta^E$  values with an effective hydrodynamic structure and water enters in the electronic zone and causes certain restrictions on its rotational, translational and kinetic motions. The TDEMTA with lower  $\eta^E$  values shows a weaker response to the hydrodynamic

Table 1. The densities,  $\rho(10^3 \text{ kg m}^{-3})$ , viscosities,  $\eta(0.1 \text{ kg m}^{-1} \text{ s}^{-1})$ , and excess viscosities,  $\eta^E(10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})$ , excess volume,  $V^E(10^{-6} \text{ m}^3 \text{ mol}^{-1})$  and excess free energy  $\Delta G^E(\text{KJ mol}^{-1} \text{ K}^{-1})$  with respect to concentration,  $c$  taken at  $10^{-4} \text{ mol kg}^{-1}$  for the dendric molecules.

$c \times 10^{-4}$	$\rho$	$\eta$	$V^E$	$\eta^E$	$\Delta G^E$
2,4,6 TDEMTA					
6.25	0.99146	7.9489	0.155	1.592	15.145
12.50	0.99148	7.9577	0.155	1.593	15.145
25.00	0.99171	7.9695	0.151	1.594	15.146
50.00	0.99181	7.9834	0.149	1.596	15.146
100.00	0.99197	7.9975	0.146	1.597	15.148
2,4,6 TCT					
2.4063	2.4049	7.9940	0.155	1.597	14.772
1.8705	1.8686	8.0007	0.154	1.597	14.772
1.4993	1.4968	8.0119	0.154	1.598	14.772
0.8319	0.8303	8.0152	0.153	1.599	14.773
100.00	0.99161	8.0182	0.153	1.599	14.774
2,4,6 TAT					
6.25	0.99133	8.0059	0.158	1.598	15.150
12.50	0.99131	8.0324	0.158	1.600	15.150
25.00	0.99153	8.0474	0.154	1.602	15.150
50.00	0.99174	8.0621	0.150	1.603	15.151
100.00	0.99180	8.0849	0.149	1.606	15.152
2,4,6 THT					
6.25	0.99147	8.0049	0.155	1.598	15.156
12.50	0.99151	8.0181	0.154	1.599	15.156
25.00	0.99155	8.0260	0.154	1.600	15.156
50.00	0.99686	8.0699	0.567	1.604	15.144
100.00	0.99732	8.0819	0.485	1.605	15.144

model with dendric water complex. It seems that the six ethyl units occupy the maximum area around the triazine ring. While the THT with three  $-\text{OH}$  groups shows moderate  $\eta^E$  values that are higher than TDEMTA but lower than that of TAT. The order for  $\rho$  values are found as  $\text{THT} = \text{TCT} > \text{TDEMTA} > \text{TAT}$  at  $6.25 \times 10^{-4}$  and  $12.5 \times 10^{-4} \text{ mol kg}^{-1}$ ,  $\text{TDEMTA} > \text{THT} = \text{TCT} > \text{TAT}$  at  $25.0 \times 10^{-4} \text{ mol kg}^{-1}$  and  $\text{THT} > \text{TDEMTA} > \text{TAT} > \text{TCT}$  at  $50.0 \times 10^{-4}$  and  $100.0 \times 10^{-4} \text{ mol kg}^{-1}$ . While for viscosities as  $\text{TAT} > \text{THT} > \text{TCT} > \text{TDEMTA}$  at  $6.25 \times 10^{-4}$ ,  $12.5 \times 10^{-4}$ ,  $25.0 \times 10^{-4}$  and  $100.0 \times 10^{-4} \text{ mol kg}^{-1}$  and  $\text{THT} > \text{TAT} > \text{TCT} > \text{TDEMTA}$  at  $50.0 \times 10^{-4} \text{ mol kg}^{-1}$  solutions. The  $\rho$  and  $\eta$  data illustrate weaker Van der Waals forces between TAT and water around lower compositions, as given in table 1, which infer attachment, a decrease in molecular activities with ethyl group while the  $-\text{OH}$  and chloro increase activities of the dendric molecule. However, for higher concentrations THT elucidate stronger Van der Waals forces behaving as a stronger structure breaker, while in TCT the weaker forces with  $\text{Cl}^-$  at around higher concentrations the weaker Van der Waals forces restrict the structure breaking action. Thus, these parameters decide the molecular behaviour of the precursors of the dendric units for the pre-cauterization, which can be used to determine the viscous properties of molecules of biophysical and biochemical interest.

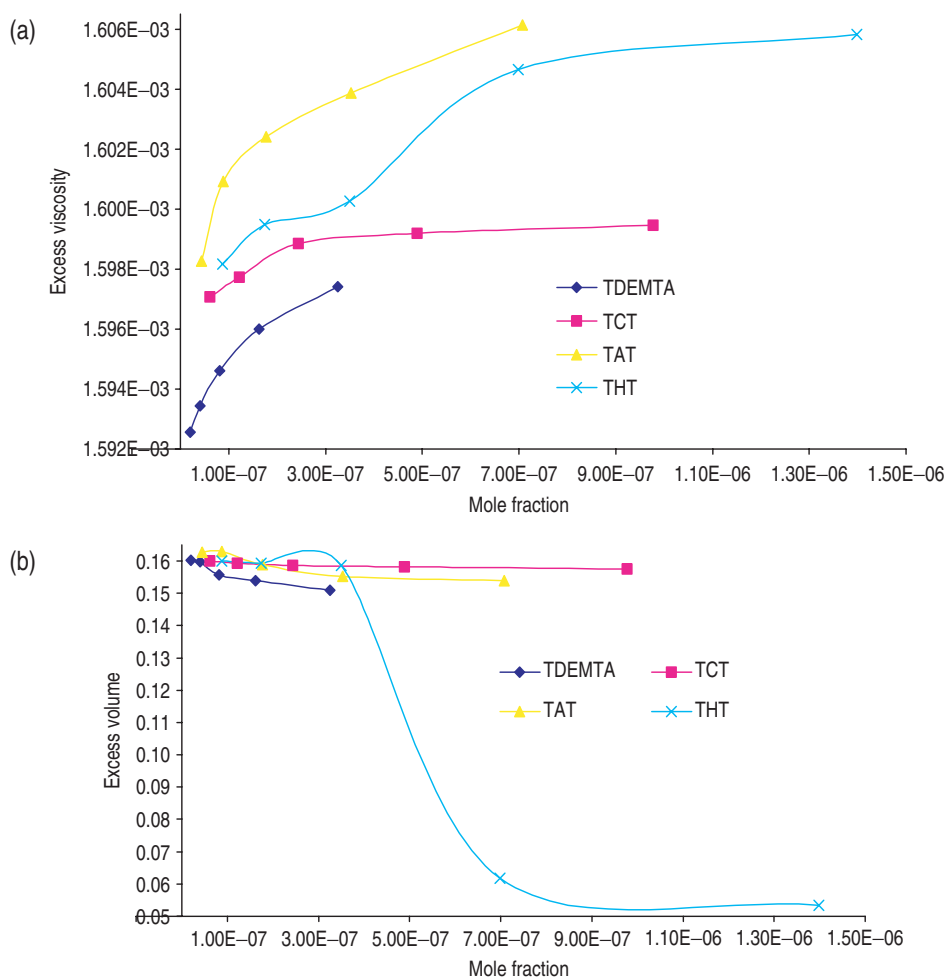


Figure 1. (a) Excess viscosities  $\eta^E$  on y-axis, (b) Excess volume  $V^E$  on y-axis, and mole fraction  $x_2$  on x-axis for 2,4,6 TCT, 2,4,6 TAT, 2,4,6 THT and 2,4,6 TDEMTA.

#### 4.2. The molar free activation energy $\Delta G^E$

We find positive values of  $\Delta G^E > 0$ , as given in table 1, which can be arranged in decreasing order according to  $\text{THT} > \text{TAT} > \text{TDEMTA} > \text{TCT}$ , with a slight decrease from  $15.148$  to  $14.772 \text{ kJ mol}^{-1} \text{ K}^{-1}$  (figure 2a and b). The higher  $\Delta G^E$  values prove that there is a weaker spontaneity towards the reaction with water i.e. it displays a weaker interaction with water, which illustrates their inability to break the hydrogen bonds of the structured water, where a cavity of water is formed on mixing then in water with the consumption of a smaller amount of energy. The TCT shows lowest  $\Delta G^E$  with maximum spontaneity with water; perhaps the electron density of chloride group favours for this action. However, the  $\Delta G^E$  values for TDEMTA, TCT and TAT shows a slight increment by  $0.02 \text{ J mol}^{-1} \text{ K}^{-1}$  in the values, but for THT the  $\Delta G^E$  values are higher than those of the others at around  $4.0 \times 10^{-7}$  mole fraction with a sharp decrease up to  $6.0 \times 10^{-7}$  mole

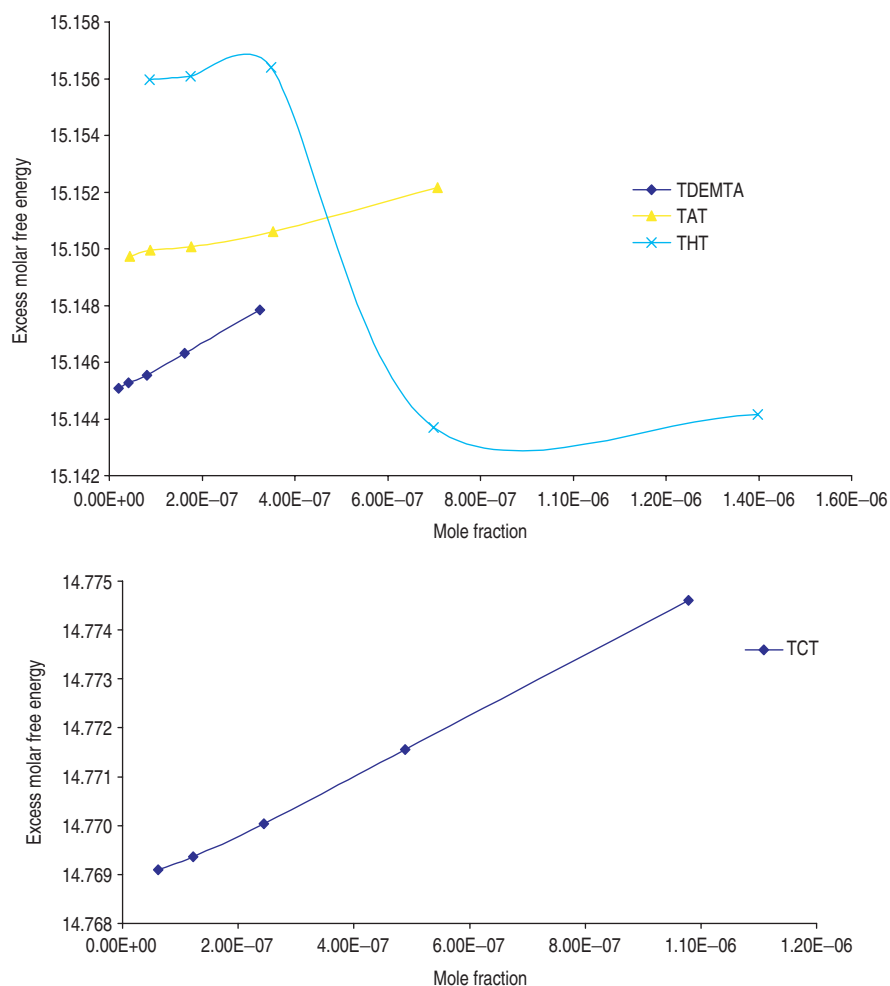


Figure 2. (a) Excess molar free energy  $y$ -axis, for 2,4,6 TAT, 2,4,6 THT and 2,4,6 TDEMTA (b) Excess volume  $V^E$  on  $y$ -axis for TCT, 2,4,6, and mole fraction  $x_2$  on  $x$ -axis.

fraction and further increase slightly from  $6.5 \times 10^{-7}$  to  $1.4 \times 10^{-6}$  mole fractions which illustrates a possibility of a micelle formation. This concentration of THT probably accumulates the larger molecules of THT with three  $-\text{OH}$  groups forming hydrogen bond. The sharp decrease in the  $\Delta G^E$  values denotes the higher spontaneity for solubility of the THT in water, which proves the development of stronger hydrogen bonds with water. The  $\Delta G^E > 0$  values of the systems suggest a dominance of the hydrophobicity which resists their spontaneous mixing. Slightly lower  $\Delta G^E$  magnitudes for the TDEMTA units are comparatively stronger bond breaker, in fact the positive  $\Delta G^E$  values show a net gain of energy from the water to get reoriented for their optimization. Thereby the cage formations of water molecules around their hydrophobic part except THT, where slightly smaller  $\Delta G^E$  value consumption for TDEMTA infer its inability to break the water structure and hence, water is not a suitable solvent for their

solubilization. This proves that the six sites of TDEMTA are blocked with ethyl groups, which restrict this interaction.

### 4.3. The excess volume $V^E$

The  $V^E > 0$  values found in order (figure 1b) of THT > TAT > TCT > TDEMTA having the  $V^E$  values in a range of 0.048–0.158 m<sup>3</sup> mol<sup>-1</sup>. Unlike the  $\eta^E$  and  $\Delta G^E$  values, the  $V^E$  values are attributed to their electrostatic structure, where the lower values depict a dominance of hydrophobic interactions. The  $V^E$  values given in table 1 for the THT increase from  $0.75 \times 10^{-7}$  to  $4.0 \times 10^{-7}$  mole fraction, and further decreases up to  $9.0 \times 10^{-7}$  mole fraction denotes the weakening in heteromolecular forces with mole fractions, and –OH group cause an effective electrostatic pressure on triazine ring; this model of forces apply an internal pressure on molecules. This illustrates an occurrence of the THT–THT interactions with a concentration weakening the electrostatic forces of the THT and water. However, the increase from  $4.0 \times 10^{-7}$  to  $1.4 \times 10^{-6}$  mole fraction in the  $V^E$  values explains the strengthening of intermolecular forces. The similar order of the  $V^E$  values is noted for TAT, while the  $V^E$  values of TDEMTA continuously decrease with mole fractions where the three nitrogen atoms in the ring and six oxygen in the side chains permit the pairwise interaction. This enhances the polarity of the solutions developing stronger TDEMTA–TDEMTA molecular interactions. But the TCT produces almost similar  $V^E$  values with mole fractions. It infers that the three chlorides in the ring of TCT do not have a stronger dipole moment, and hence denotes a slightly weaker interaction when compared to others.

## 5. Conclusions

In our study, the TCT, TAT, THT and TDEMTA molecules have been used as dendric units, where their molar fraction or concentration directly predicts the electrostatic forces, which represents for binding these dendritic units for the preparation of larger-chained dendritic unit or the stability of the binding among the units being used for the dendrimer molecules preparation. Thus the  $V^E$  functions are significant to predict the spontaneity of these molecules to enhance or inhibit the molecular growth of the dendrimer unit also. Such study through a light on their binding mechanism, potentiality as they may be used as legend, with resin may develop a heat resistant, thermoplastic material. The basic nature of the molecules comprises of the hydrophobicity and the hydrophilicity of the precursor units in the aqueous solution, and thus functions to predict the feasibility of the preparation of any higher branched dendrimer.

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