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Molecular Mechanics Study on the Interaction of MMA with Higher Alcohols and Organic Solvents

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Abstract

Computer simulations have enabled fast, accurate and simple study of the structure and bending in small and macromolecular systems. In particular, the solute-solvent interaction studies have been made easy by molecular modeling with computers. The miscibility behavior of binary mixtures of MMA with various solvents viz., aromatic ether, halogens and alcohols at 303 K is studied using molecular simulation technique. The results were compared with the experimental ultrasonic techniques and are found to be in good agreement.

KeyWords: MMA, molecular mechanics, interaction parameter (χ), excess viscosity (η^E).

Introduction

This paper deals the application of modeling methodology to understate the local interactions between solute and solvent from their interaction energies and coordination numbers by the application of Cerius2 Blends module. Finding a complex mixture is the most challenging one for the successful product formulations. So that it is very important to give attention on the properties like compatibility, miscibility, mixing and adhesion in the development of innovative, value-added products.

Information on the miscibility of polymers with solvents or their adhesion to one another is necessary for several industrial and commercial applications. Some of the applications are polymer mixture processing[1,2] identification of plasticizers and swelling agents, preparation of membranes[3] and phase separation processes. The properties of polymer-polymer and polymer-solvent interfaces are crucial in understanding the miscibility and adhesion properties. Due to inherent difficulties, the experimental data on these systems are limited. Hence, atomistic simulation studies on these systems are significantly important.

Usually, these modeling techniques have been used only for oligomers / polymers and polymer-mixtures. For the first time this modeling technique is used for predicting the thermodynamical parameters and the nature of intermolecular interactions of binary mixtures of a monomer – Methyl Methacrylate (MMA) with six solvents *viz.* anisole, trichloroethylene, tetrachloroethylene, 2-chloroethanol, iso-butanol and tert-butanol at 303K. A great deal of literature is available on the physical, chemical properties of PMMA and miscibility behavior of MMA by theoretical approach[4-7]. Huang et al[8] have also studied the behaviour of binary mixtures through molecular modeling and simulation studies. MMA is a monomer, which has also a wide range of application in the field of medicine and industrial area. MMA is a thermoplastics used in industry and dentistry.

One among the important application of MMA is, for a synthetic polymer it act as an excellent alternate for glass. The suitability of MMA for different applications has been investigated in detail[9,10].

Material and Methods

Building and sketching a model of the solute and solvent molecule is done with built-in *chem draw* tool. For this, the feeding parameters are the number of atoms involved *viz.* number of carbon, hydrogen, oxygen and chlorine atoms. Using the Discover Package, energy minimization is done for solute and solvent molecules to optimize the geometry of the base molecule. The minimized structures were further used to compute the pair interaction energies using the Blend module implemented in Cerius[2] package following the method suggested by Fan and coworkers[11]. The structures obtained after minimization for MMA and the six solvents are shown in figure 1–7. Construction of the required binary mixture (combination of solute – solvent pair) is made for further calculation. *i.e.* several pairs with different relative orientation of the solute-solute, solute-solvent, solvent-solute and solvent-solvent were generated and their interaction energies were computed The possible cluster formation between the like and unlike molecules is also taken as snap shots are shown in figure-8-14. The calculations are done for a set of conditions such as temperature, vapour phase and number of iterations to be done. This pair wise interaction was calculated for 10,000 pairs in each case. For each set of interactions, 500 clusters were generated and average co-ordination numbers for various binary systems such as solute – solute (z_{11}), solvent-solvent (z_{22}), solute-solvent (z_{12}) and solvent-solute (z_{21}) were calculated.

Running the calculations (pair interaction energies *viz.* solute-solute, solute-solvent, solvent-solute and solvent-solvent - E_{11}, E_{12}, E_{21} and E_{22} is done using Monte Carlo approach. This methodology has been used by various researchers for different solutes and solvents[9-13]. Using the values of interaction energies (E_{ij}) and the coordination numbers (Z_{ij}), the computation of interaction parameter (χ) is made.

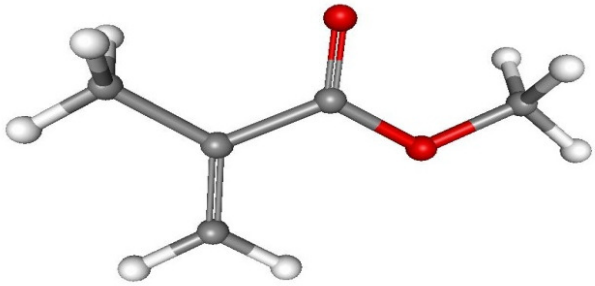

Figure-1
Methyl Methacrylate (MMA)

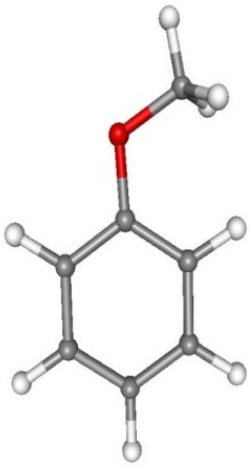

Figure-2
Anisole

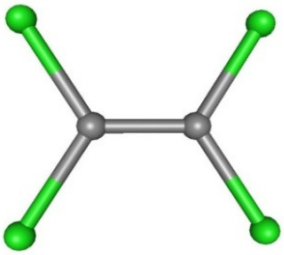

Figure-3
Tetrachloroethylene

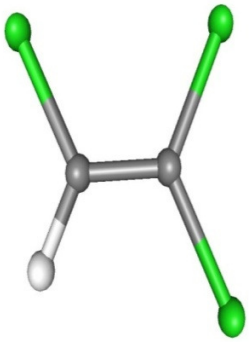

Figure-4
Trichloroethylene

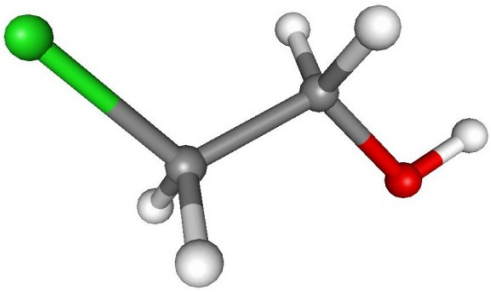

Figure-5
2-chloroethanol

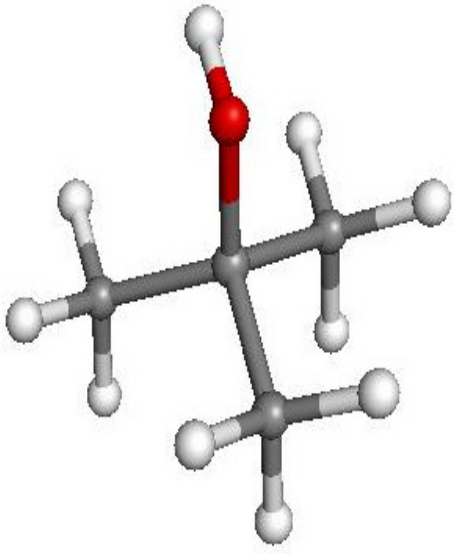

Figure-6
tert-butanol

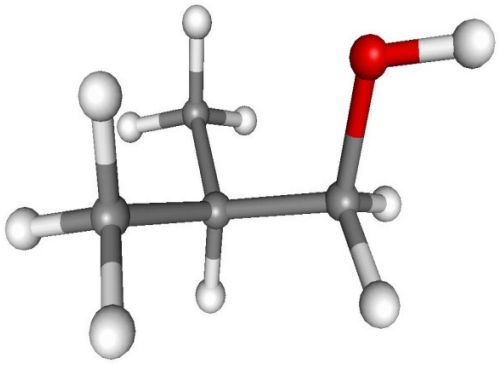

Figure-7
Iso – butanol

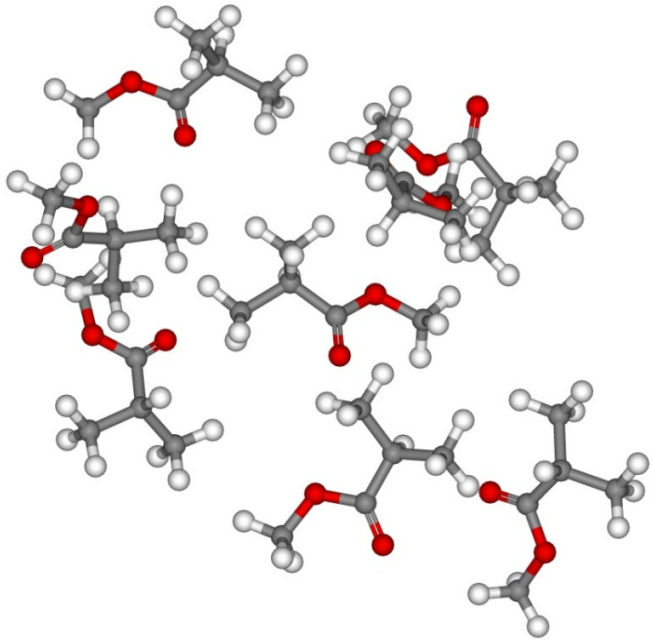

Figure-8
MMA cluster

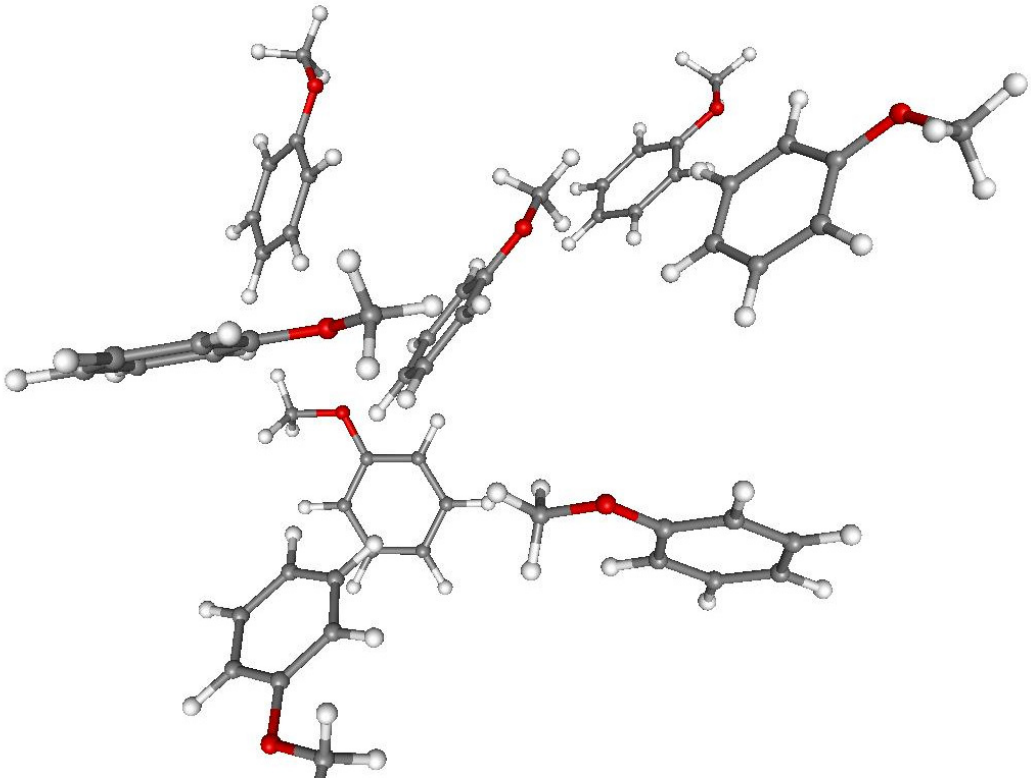

Figure-9
Anisole cluster

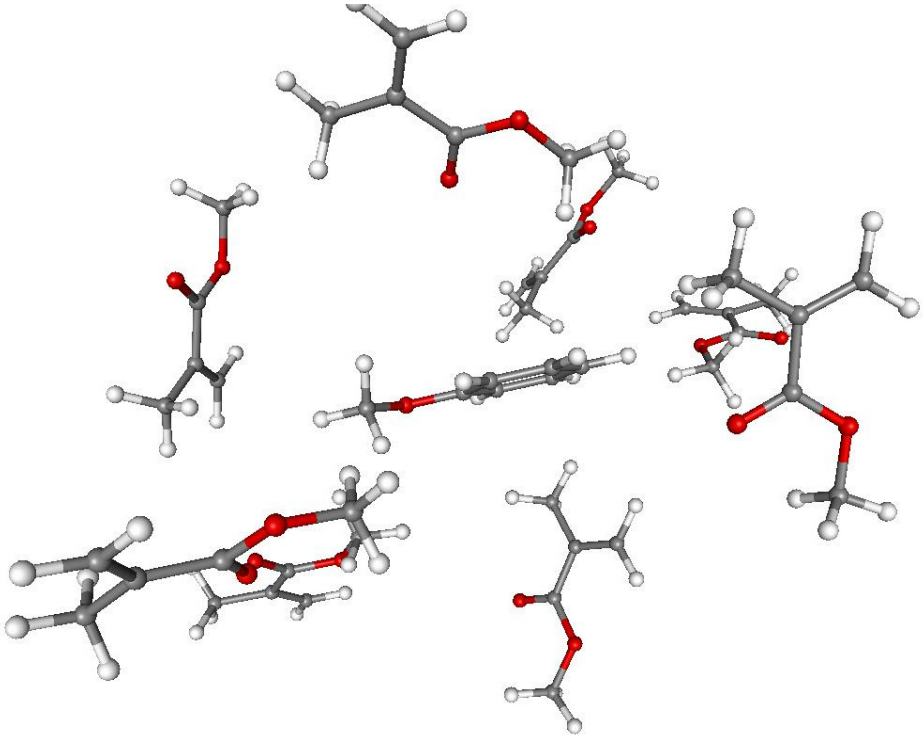

Figure-10
Anisole atom surrounded by MMA cluster

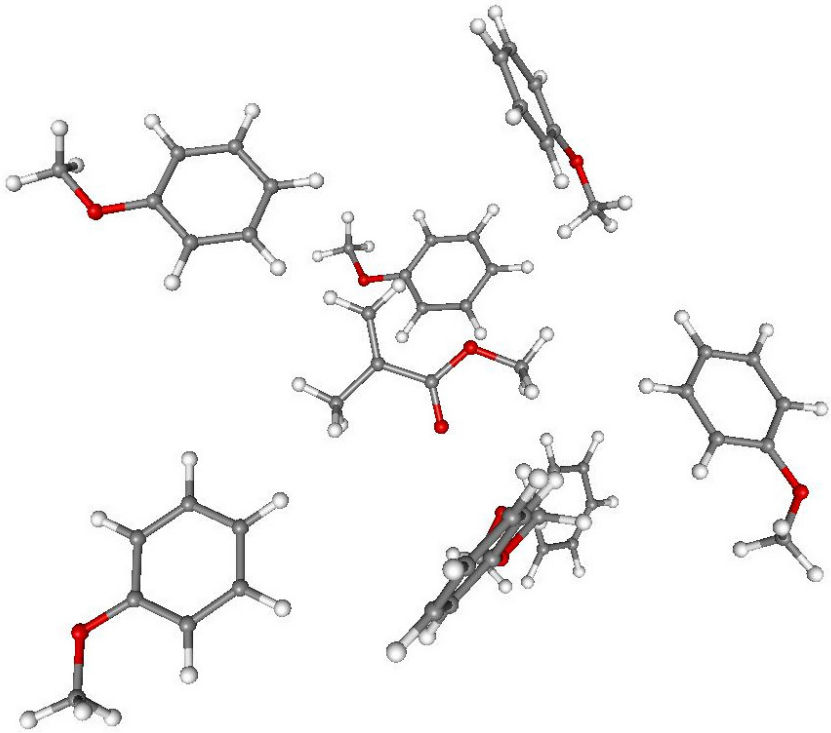

Figure-11
MMA atom surrounded by anisole cluster

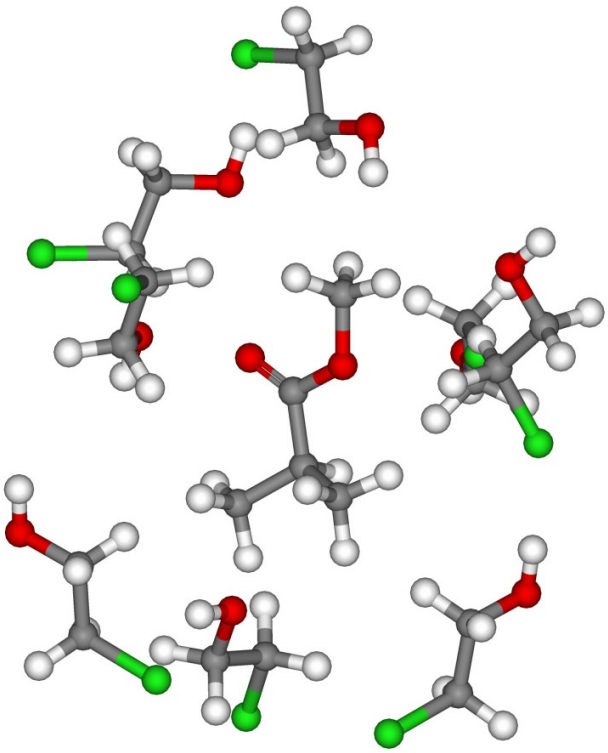

Figure-12
MMA atom surrounded by 2-chloroethanol cluster

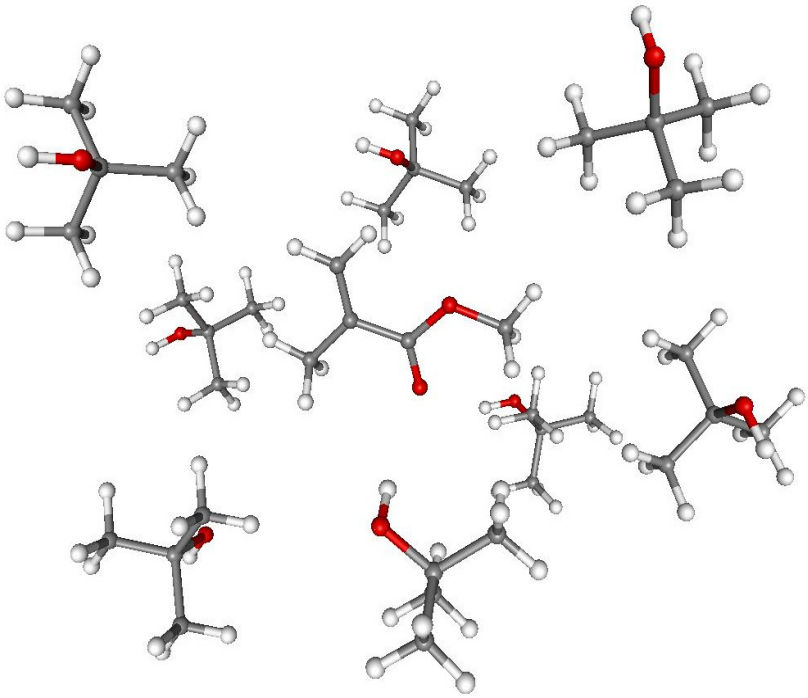

Figure-13
MMA atom surrounded by tert-butanol cluster

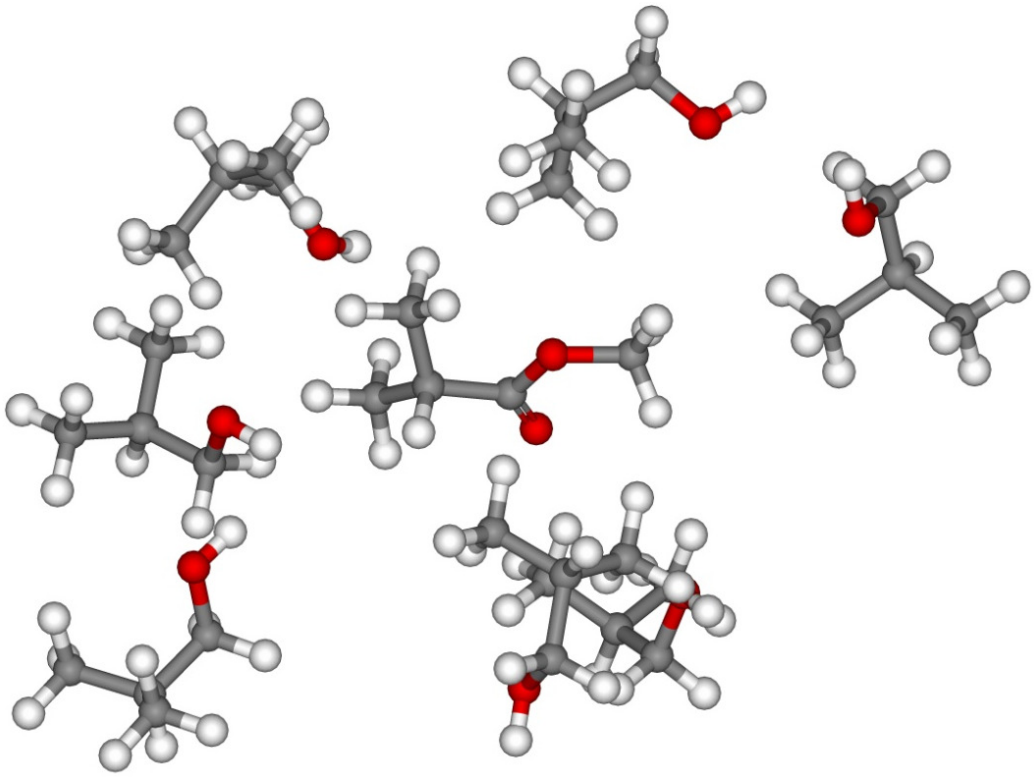

Figure-14
MMA atom surrounded by iso-butanol cluster

Usually the miscibility of a substance is determined by the energy of mixing. So that in this study, the miscibility and the Flory-Huggins 'χ' parameter of MMA (monomer) can be estimated from the energy of mixing parameters (ΔE_{mix} or (ΔE_{AB}), which is dominated by the local interactions between monomer segments and molecules of solvent.

$$\Delta E_{mix} = E_{AB} - 0.5 (E_{AA} + E_{BB}) \quad (1)$$

For the value of $\Delta E_{mix} > 0$, materials are incapable to form a stable blend thermodynamically. For the value of $\Delta E_{mix} < 0$, materials may capable to form stable blend. From these thousands of molecular pairs which were obtained from the Monte Carlo simulation Interaction energies are calculated by evaluating their energies. Coordination numbers come from a similar simulation that generates thousands of clusters. Z is the co-ordination number and E_{AB} is the interaction energy between molecular pair A and B. From the above values, the interaction parameter 'χ'[9] is given as

$$\chi = \frac{Z_{AB}\Delta E_{AB}}{RT} \quad (1)$$

In the above equation 1 Z_{AB} represents the number of nearest neighbors (of species A) coordinating with B, than any other Z (Z_{BA}, Z_{AB} etc.,) or their combinations. The differential energy ΔE_{AB} is given by[9]

$$\Delta E_{AB} = 0.5 (E_{AB} + E_{BA}) - 0.5 (E_{AA} + E_{BB}) \quad (2)$$

Flory-Huggins theory defines χ_{FH} or (χ) like a Hilderbrand interaction parameter of the form B/T [14]. In the case of polymer blends an entropic component A is necessary, thus making χ_{FH} = A+B/T. Various theories have been attempted to account for this type of non-combinatorial entropy, like the one that uses equation of state theory employing changes in density[15].

Results and Discussion

The interaction parameter is calculated using the equation 1 with the coordination number and the interaction energy as input parameters. The coordination numbers (Z_{12}, Z_{21}) for the interactions of various solvent molecules with MMA represents the number of solvent molecules that can coordinate with MMA and quantifies the interaction between the polymer and solvent systems. Using these parameters, the interaction parameter has been computed employing equation 1. The calculated χ values are displayed in table-1 along with change in interaction energies (ΔE_{AB}). It can be seen from table 1 that the values of χ corresponding to the MMA mixtures changes due to increase in the potential interaction sites with the solvent molecules. The visualization of solute-solute interactions, solute-solvent interaction, solvent-solute interaction and solvent – solvent interaction for MMA + anisole mixture are given in figure 8-11.

All the figures show the different types of clustering and the possibility of interactions among the unlike molecules. The different nature of interactions and the effect of dispersive forces may also be clearly seen from these figures. Figure 12–14 shows the interaction of MMA with alcohol molecules (solvent – solute type). These figures are also in conformity with the predictions of Dharmalingam and others[16] on MMA + alcohol mixtures, by FTIR studies. They have found that the specific interactions between the monomer (methyl methacrylate) and the —OH group of alcohol are possible. At the same time non-specific dispersion interaction between the alcohol molecules are also possible. But both are in opposing trend.

Belmares *et. al.*[17] calculated the solubility parameter of MMA from the measured ΔE_{AB} values by Molecular Dynamic simulations. Their findings with MMA are in agreement with the values obtained in this report. ΔE_{AB} values are negative for MMA + anisole, MMA + tetrachloroethylene mixture, and zero for MMA + trichloroethylene mixture. These values indicate the extent of miscibility of MMA in these solvents. A large negative value of χ for anisole implies better miscibility among the six binary mixtures. It can be observed that χ values are positive for alcohol mixtures (MMA + 2-chloroethanol, MMA + tert-butanol and MMA + iso-butanol). It shows that miscibility is more for non-alcohol mixtures than for the alcohol mixtures. This trend is well supported by the experimental value of excess viscosity (η^E) studies shown in figure-15. For the three non-alcohol binary mixtures, the excess viscosity values are positive showing that the dispersion forces are less. For the alcohol mixtures, the excess viscosity values are negative suggesting that the dispersion forces are more.

Table-1
The value of interaction parameter χ for binary mixtures at 303K

System	Interaction energy E_{11}^* = -2.01						
	E_{12}	E_{21}	E_{22}	Z_{12}	Z_{21}	ΔE_{12}	χ
Anisole	-2.52	-2.51	-2.1	7.51	7.61	-0.46	-5.75
tetrachloroethylene	-1.89	-1.88	-1.59	7.84	7.22	-0.085	-1.06
trichloroethylene	-1.69	-1.72	-1.4	8.27	6.87	0.00	-0.00
2-chloroethanol	-1.54	-1.55	-1.3	8.57	6.52	0.11	-1.37
tert-butanol	-1.57	-1.56	-1.36	7.81	6.97	0.12	-1.47
iso-butanol	-1.62	-1.6	-1.51	7.84	7.02	0.15	-1.84

* Interaction energy E_{11} = -2.01 is same for MMA

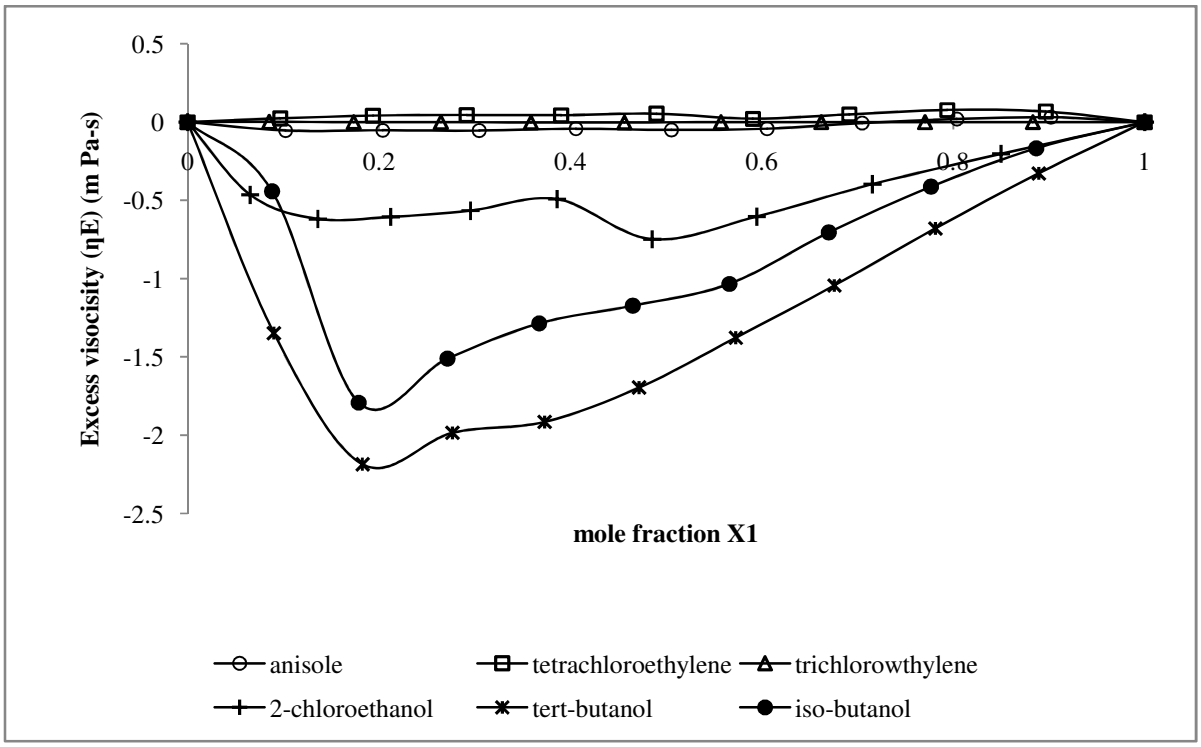

Figure-15
Variation of excess viscosity (η^E) *vs* mole fraction of MMA (X_1) for all binary mixtures at 303 K

Conclusion

Thus in this paper, the application of the Molecular Mechanics (MM) studies, usually done for macromolecular systems, is adopted for MMA monomer mixtures with six solvents. The results obtained indicate suitability of the MM studies. In addition, the parameters like pair interaction energies and interaction parameter calculated in this report are found to be in agreement with earlier reports in literature. In addition, the experimental finding on excess properties is in agreement with the predictions of the theoretical calculations of this chapter.

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