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The possible formation of nano-clusters of succinic acid and maleic acid in tetrahydrofuran due to incomplete solvation

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In continuation of our work on the conformational analysis of succinic acid (SA) and maleic acid (MA) in different solvents, we present here the experimental dielectric and IR and also the *ab initio* Hartree–Fock calculations of the two dicarboxylic acids in tetrahydrofuran (THF). The dielectric measurements are carried out at microwave X-band frequency of 9.7 GHz and the calculations are performed at STO-3G and 6-31G(d) basis sets. The dielectric data and the dipole moment determined experimentally are compared with the dipole moment determined from the conformal analysis. It is seen that the dielectric properties of SA/MA in THF are much different from that of SA/MA in 1-4, dioxane (1-4D) that we had reported previously. The IR spectra of SA–THF system is also reported here. The present study indicates the possible formation of nano-clusters of SA/MA in THF due to incomplete solvation by THF.

Keywords: Dielectric spectroscopy; Succinic acid; Maleic acid; Nano-cluster; THF; Ab initio

1. Introduction

The study of small molecules in dilute solutions of different solvents is one of the methods for the estimation of short-range ordering that will exist in these molecules when they are in either a polymeric form or in a cluster of many molecules [1]. The different species of molecules interact by means of polarisation effects through the formation of intra molecular and inter molecular bonds. Chemical and biological activities of a system are related to the transfer of electron/proton in the system and the dipole moment is a measure of the electronic charge transfer. The electric dipole moment μ of a molecule is a quantity of fundamental importance in structural chemistry [2]. The dipole moment is further important in Quantitative Structure Activity Relationship (QSAR) and Quantitative Structure Property Relationships (QSPR) that are integral to rational design methods where it is assumed that the biological activity can be represented as a function of the measurable physio-chemical properties. One of the many parameters used in QSAR and QSPR is the dipole moment of the system.

There are many spectroscopic and computational methods for the determination of the electronic charge distribution in a molecular species, but it is seen that

a combination of experimental methods and simulations gives better results by reducing the ambiguity in interpreting the results [3]. This concept gains further importance when the system under study is in the solution state where the entire system is in a state of dynamic equilibrium. Use of such combined methods of study are even more important in the presence of hydrogen bonding since hydrogen bonding leads to small but significant changes in the physical and chemical properties of the system. Further, hydrogen bonds have typical energies between 2 and 5 kcal/mol, and hence are in a dynamic make-and-break state at room temperatures.

Dielectric spectroscopy is a valuable tool of the determination of dipole moments in the solution state since the samples are easy to prepare and there is no need for an additional molecular species as a marker such as those in NMR. Further the rotational frequencies of small molecules fall in the microwave frequencies; the study of the dielectric response at microwave frequencies often yields a wealth of information regarding the molecular dynamics and the electronic charge distribution of the system under study.

We present here the dielectric, IR and HF calculation results of two dicarboxylic acids, namely succinic acid

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(SA) and maleic acid (MA) in tetrahydrofuran (THF) solvent. This is a continuation of our previous work on SA and MA in 1,4-dioxane (1-4D) [4]. The motivation for the present work has been to study the effect of change of solvent from a six-member ring with two oxygens in 1-4D to a five-member ring with one oxygen in THF on the dielectric and conformational properties of SA/MA in solution.

It has been noted that SA tends to have a predominance of the gauche conformation in the dilute solutions [5] although this is the energetically lesser favourable conformer. MA has a C=C double bond, rendering the molecule to have conformational constraints as compared to SA. Hence, the choice to study both SA and MA together. THF is an aprotic solvent with a dielectric constant of 7.57 and refractive index of 1.407. While the conformational analysis and comparison of the experimental data with that of calculations for the IR and Raman spectra for THF have been reported previously, there is practically no data interpreting the experimental dielectric results in terms of conformational analysis.

Previous studies on the solvation of SA by water and THF have indicated the possibility of incomplete solvation of SA by THF and that THF may not be able to break the intramolecular hydrogen bond that exists in SA to convert it to a more favourable trans conformer. A detailed analysis of the pseudo-rotation of THF has been studied by *ab initio* methods [6]. Due to the pseudo-rotation that takes place in five-member ring structures, THF has three possible envelope and twist forms [7]. The barrier is seen to be about 0.4 kcal/mol. In the present study, the minimum energy conformer is similar to the C_{2v} symmetry structure of Rayon *et al.* and was taken up for all calculations.

2. Experimental and computational details

The experimental and simulation methods are as reported previously [4]. Solutions of succinic and MA in THF were prepared in the concentration range of 0.01–0.05 weight fractions. The chemicals were of purity >99.5% and were used without further purification. The static dielectric permittivity was measured using a LCR meter, ϵ' and ϵ'' were determined at X-band frequency (9.7 GHz) using a microwave test bench plunger method and ϵ_∞ was determined from refractometry studies with sodium-D source using an Abbe's refractometer. The measurement accuracies of ϵ' and ϵ'' , the real and imaginary part of the dielectric permittivity, are ± 1 and $\pm 5\%$ respectively. The relaxation times were determined using Higasi's equations, and the bistable model of Eyring was considered for the rotational dynamics of the molecules; the details are identical to those described previously [3,8].

For molecular modelling of hydrogen-bonded complexes, MNDO/PM3 is found to be the most appropriate among the semi-empirical methods [9]. Conformational analysis for the chosen systems was performed initially at the PM3 optimisation using WinMOPAC, the output of which was taken for subsequent optimisations at STO-3G

and 6-31G(d) levels. The optimisations at STO-3G and 6-31G(d) were performed using Gaussian-03 on an IBM64-RS6000 machine.

Simulations of the molecular conformations of SA/MA and THF were performed with an intention to enhance the understanding of the experimental results. This is especially important for the studies in the liquid state where there are no systematic theories to completely understand the experimental results. That is to say that although dielectric measurements are indicative of the microscopic interactions between the different molecules, such data cannot be interpreted directly in terms of molecular conformations. In order to enhance the understanding of the experimental results, simulations of the probable molecular conformations of the system are performed. Wherein the dipole moment of the conformer as determined from computational conformational analysis is compared with the experimental dipole moment in order to surmise the most probable conformation of the system.

There are two types of calculations that can be performed to determine the dipole moment of a solute in a solvent in the dilute regime, using Gaussian software. The first approach is that of using a simple solvation model, like that of the Onsager's solvation model wherein the solute molecule is assumed to be caged in a spherical cavity of the solvent. The dielectric permittivity of the solvent is an important parameter for this calculation since the strength of the permittivity decides the extent of polarisation of the solute molecule. The dielectric permittivity of the solvent as determined from our experiments, i.e. $\epsilon' = 7.14$ is fed to the program in order to calculate the effective radius of the solvent. The calculation of the effective radius of the solvent molecule is done using the inbuilt function of Gaussian. But Onsager's model is a rather simplistic model and hence it is possible that calculations performed using this model does not always reflect the experimental results, such as in the present case. Hence an attempt was made in the present case to study some of the possible interactions between the solute and the solvent molecules using an *ab initio* energy minimisation routine and see if any of the simple calculations can predict the experimental results.

Two different calculations are reported in this paper (a) solvation of the solute molecule by Onsager's reaction field model and (b) calculation of the dipole moment of specific solute–solvent interactions. Calculations of specific SA/MA interactions with THF are complete analysis in themselves. The minimum energy conformations were determined at lower basis sets and the final calculations were carried out at 6-31G(d) basis set and are reported here. The dipole moment corresponding to each of the conformations is compared with the value determined from experiments so as to identify the possible interactions of the given system.

The geometric optimisations for SA/MA in 1-4D at STO-3G and 6-31G(d) basis sets are as reported previously by us [3]. THF is known to have several conformations [10] with the main feature being a puckering of the ring.

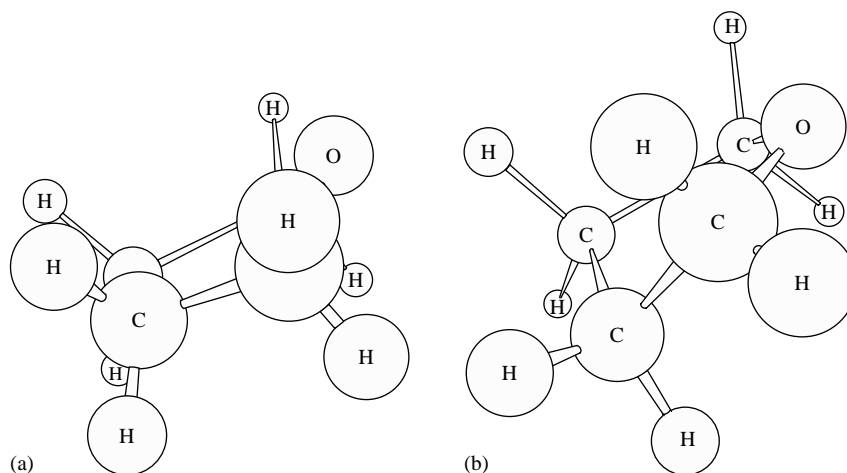


Figure 1. Optimised geometry of THF at (a) STO-3G basis set and at (b) 6-31G(d) basis set.

In the present study geometric optimisation of THF was performed at STO-3G and also at 6-31G(d) basis sets. The resultant structure at STO-3G and 6-31G(d) basis are shown in figure 1(a) and (b) respectively.

For the stable conformers, the Onsager's model reaction field was applied with THF as the solvent. In this model, it is assumed that the solute is placed in a spherical cavity in the solvent. The solvent is taken to be a homogeneous polarisable medium that has a constant dielectric permittivity. This is a simple model wherein the dipole moment of the solute molecule polarises the surrounding medium, which in turn polarises the solute charge distribution. In Gaussian-03 [11], this mutual polarisation is treated in a self-consistent manner. The effective volume of the solvent was determined using the software, before the reaction field calculations were performed. The reaction field is given by the equation 1

$$R = \left[\frac{2\mu(\epsilon - 1)}{V(2\epsilon + 1)} \right] \quad (1)$$

Where V is the volume of the solvent molecule, μ the dipole moment of the solute and ϵ the permittivity of the solvent.

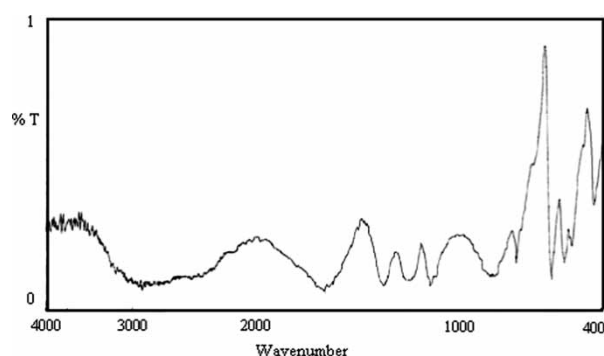


Figure 2. IR spectrum of the succinic acid (solute). Transmission is in arbitrary units and wave number in cm^{-1} .

The IR spectrum in the $400\text{--}4000\text{ cm}^{-1}$ range was recorded using Jasco FT/IR 5300 for pure SA, THF and the solution of SA in THF (5% by weight). The spectra are shown in figures 2–4.

3. Results

The relaxation times τ_1 and τ_2 of SA/MA in THF are reported in tables 1 and 2 and they show trends that are unlike those seen in SA/MA in 1-4D [4]. In the present studies, it is seen that the overall relaxation time τ_1 decreases with increasing concentration of SA/MA where as in 1-4D, τ_1 increased with increasing concentrations of SA/MA. Further the absolute values of τ_1 in both the cases

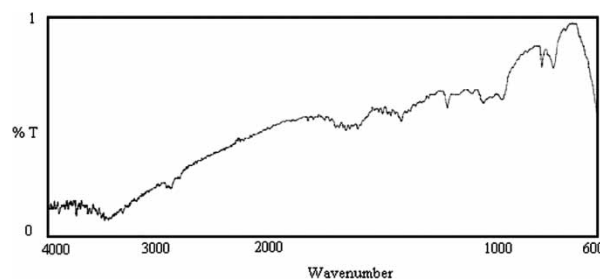


Figure 3. IR spectrum of the THF (solvent). Transmission is in arbitrary units and wave number in cm^{-1} .

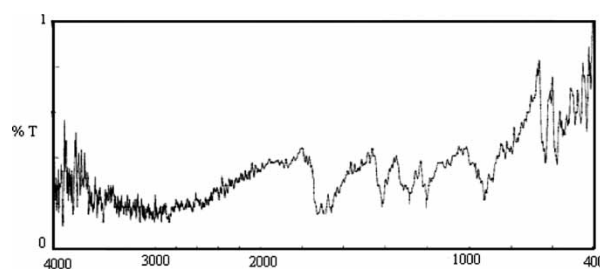


Figure 4. IR spectrum of the succinic acid + THF (solution). Transmission is in arbitrary units and wave number in cm^{-1} .

Table 1. Static (ϵ_∞), high frequency (ϵ_∞), real (ϵ') and imaginary (ϵ'') parts of the dielectric permittivity, relaxation times (τ) and dipole moment (μ) of MA in THF.

Weight fraction	ϵ_0	ϵ_∞	ϵ'	ϵ''	Relaxation time			μ (D)
					τ_1 (ps)	τ_2 (ps)	τ_0 (ps)	
0.01	7.94	1.98	7.62	2.98	565.1	1.7	31.0	1.62
0.02	8.22	1.99	7.71	3.11	304.0	2.6	28.0	1.64
0.03	8.53	2.01	7.89	3.26	162.3	3.2	22.7	1.66
0.04	8.70	2.02	8.13	3.34	96.5	2.8	16.3	1.67
0.05	8.92	2.03	8.36	3.44	71.4	2.6	13.7	1.68

Table 2. Static (ϵ_0), high frequency (ϵ_∞), real (ϵ') and imaginary (ϵ'') parts of the dielectric permittivity, relaxation times (τ) and dipole moment (μ) of SA in THF.

Weight fraction	ϵ_0	ϵ_∞	ϵ'	ϵ''	Relaxation time			μ (D)
					τ_1 (ps)	τ_2 (ps)	τ_0 (ps)	
0.01	8.05	1.98	7.69	3.03	321.0	1.97	24.9	1.79
0.02	8.34	1.99	7.78	3.18	208.6	2.83	24.3	1.80
0.03	8.59	2.01	7.83	3.29	197.3	3.73	27.15	1.82
0.04	8.92	2.02	8.12	3.45	101.0	3.75	19.49	1.82
0.05	9.33	2.03	8.41	3.65	70.8	4.00	16.94	1.83

are very different. Molecules solvated by THF show larger τ_1 relaxation times compared to those solvated by 1-4D. τ_2 on the other hand is seen to increase with increasing concentrations of SA/MA on solvation by both THF and 1-4D. The values of τ_1 and τ_2 are comparable in solutions of 1-4D where as they are different in solutions of THF. It is known that the intra molecular and inter molecular rotations can be resolved if $\tau_1/\tau_2 > 10$ [12]. Since this holds in the case of SA/MA solvated by THF, it can be concluded that there are two distinct rotations occurring in these systems namely the rotation of the smaller THF molecule and that of a larger cluster. Further, the dipole moment of SA/MA on solvation by THF is considerably lower than that when solvated by 1-4D. Since the solutions of SA/MA in both the studies are in the dilute regime, it is assumed that the molecules of SA/MA do not exist as very large clusters. Also, the solution of SA/MA did not show

any visible particulates. Since there is a positive indication of a cluster formation and at the same time the presence of very large clusters are ruled out, it is concluded that the clusters formed are nano-sized.

The overall relaxation time of THF was found to be 3.2 ps at 35°C by time-domain experiments [13]. It can be seen that in the present case τ_2 roughly corresponds to the relaxation time of THF alone. This indicates that in the solvation of SA/MA by THF, the THF molecules may not be strongly bonded to SA/MA, hence enabling the THF molecules to undergo independent molecular rotations. This could thus lead to incomplete solvation. The STO-3G simulation results for SA/MA and THF and their solvation is given in table 3 and the results at 6-31G(d) are given in table 4. It can be seen from the results that the estimated values for the dipole moment of the SA/MA systems in THF are far greater than the experimental values.

Table 3. Total energy and the dipole moment at STO-3G optimisation.

System	μ (gas phase) (D)	Total energy (gas phase) (Hartree)	μ (on solvation) (D)		Total energy (on solvation) (Hartree)
			THF	1-4D	
THF	1.5178	- 228.1510030	-	-	-
Succinic acid—Trans	5.6105	- 448.4528787	4.2746	5.8418	- 448.0376825
Succinic acid—gauche	3.6181	- 448.4699261	4.6964	4.5608	- 448.4460061
Maleic acid	3.2337	- 447.2297874	2.0607	3.7741	- 447.2141982

Table 4. Total energy and the dipole moment at 6-31G(d) optimisation.

System	μ (gas phase) (D)	Total energy (gas phase) (Hartree)	μ (on solvation) (D)		Total energy (on solvation) (Hartree)
			THF	1-4D	
THF	1.9386	- 230.9764462	-	-	-
Succinic acid—trans	6.1563	- 454.4457889	6.4588	6.0959	- 454.0295712
Succinic acid—gauche	6.1544	- 454.4457889	6.9407	5.4503	- 454.4534150
Maleic acid	6.0764	- 453.2410527	2.8543	4.8249	- 453.2167701

Table 5. Some specific interactions between SA/MA and THF at 6-31G(d) basis set.

System	μ (D)	Energy (Hartree)	Figure number
Sag-(2)	6.6569	- 908.905798	5
Sag (1)-THF (1)	9.7970	- 685.440678	6
Sag (1)-THF (2)	4.1887	- 916.429027	7
Sag (1)-THF (3)	4.6664	- 1147.411740	8
SAg (1)-THF (4)	6.3112	- 1378.391990	9
SAt (1)-THF (1)	9.7987	- 685.440678	10
SAt (1)-THF (2)	4.5047	- 916.420223	11
MA (1)-THF(1)	10.8900	- 684.246145	12
MA (1)-THF (2)	10.3539	- 915.226349	13

The numbers in brackets indicate the number of molecules participating in the interaction. G refers to the *Gauche* conformation and *t* to the *trans* conformation. The figure numbers of the optimised conformers are indicated in the last column.

Since the results of the Onsager's solvation calculations did not provide a clear resolution of the nature of interactions in SA/MA in THF systems, some specific interactions of SA and MA with THF were investigated with an aim to determine a structure whose dipole moment would be close to that of the experimental value. If such a structure is found, it may be concluded that instead of the SA/MA molecules being solvated by the solvent, some specific SA/MA-THF interactions are occurring. Here the actual interactions between a specific number of SA/MA molecules with a specific number of THF molecules are calculated and no solvation model is applied. The results are reported in table 5 and the conformers are shown in figures 5-13.

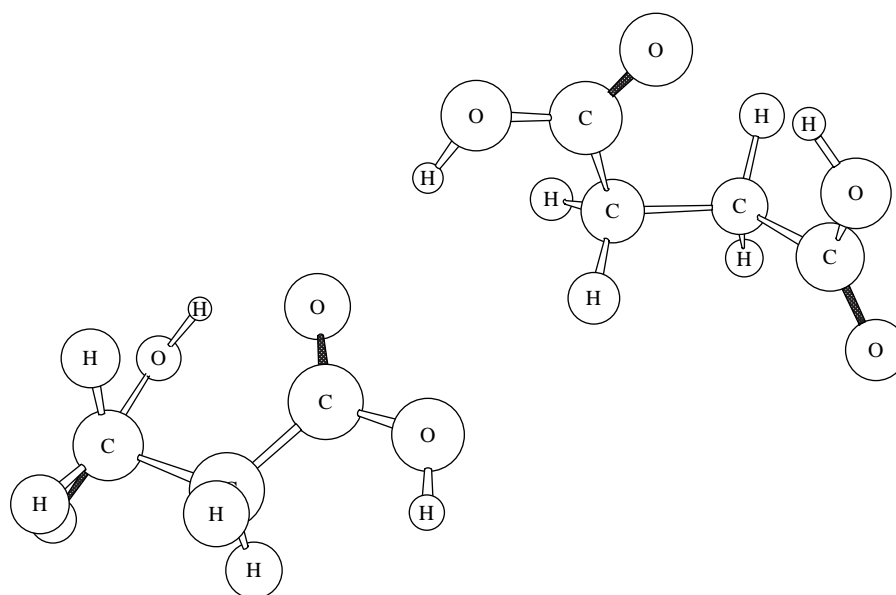


Figure 5. Optimised geometry of two molecules of Succinic acid.

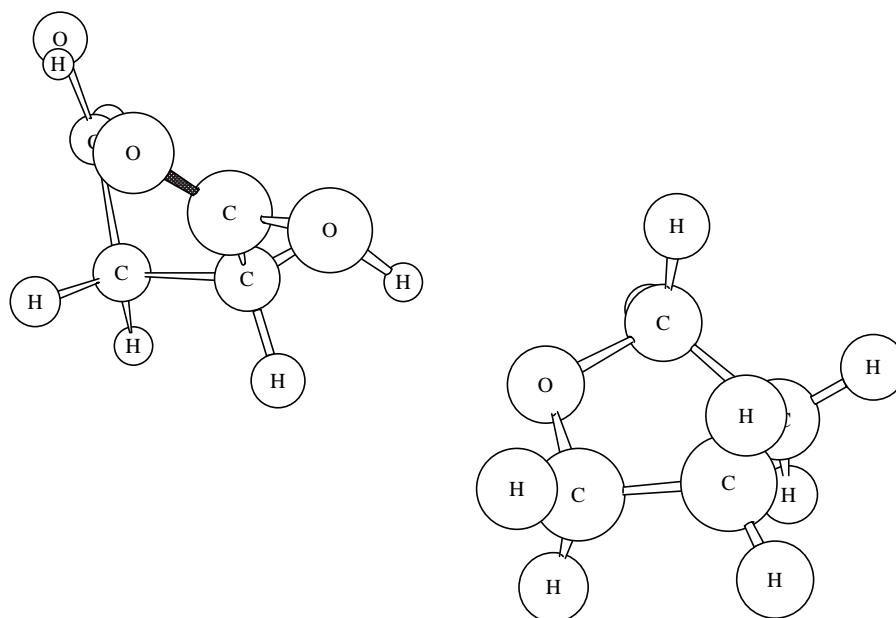


Figure 6. Optimised geometry of one molecule of succinic acid and one molecule of THF.

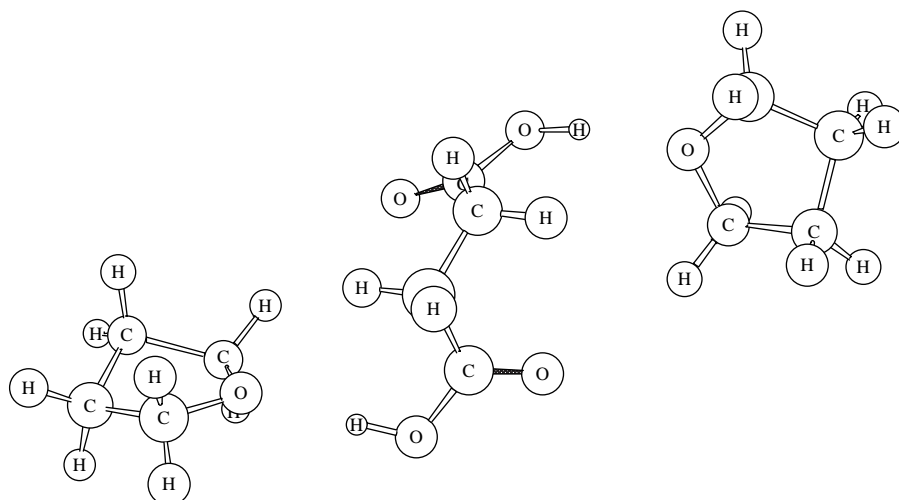


Figure 7. Optimised geometry of one molecule of succinic acid and two molecules of THF.

The results of table 5 are also not indicative of the formation of any specific SA–THF interactions between small number of molecules of SA/THF that could lead to the experimental results. Thus, it is concluded that there is no one single predominant interaction in systems of SA/MA in THF and the experimental results are possibly indicative of an average over many interactions. Since the dipole moments are vector additive, no further analysis is possible based on the available data. There are many possible configurations of the smaller nano-clusters that

can possibly lead to the experimentally observed dipole moment, with the net observed dipole moment being an average over both the molecules in the cluster and a macroscopic average over all the clusters.

There have been previous observations on the anomalous solvation by THF. Monte Carlo simulations of water–THF mixing process have shown the interaction to be exothermic at low THF concentrations. An enhancement of water–water hydrogen bonding in water–THF system compared to water–methanol systems [14].

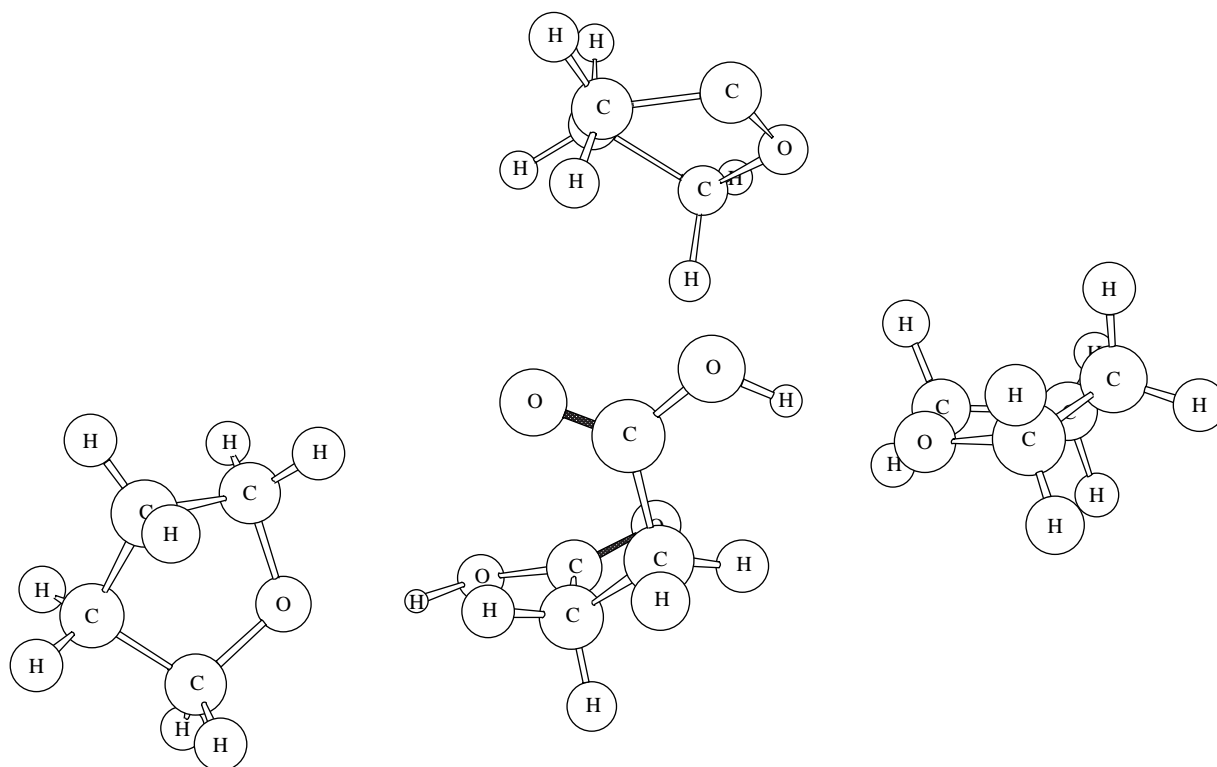


Figure 8. Optimised geometry of one molecule of succinic acid and three molecules of THF.

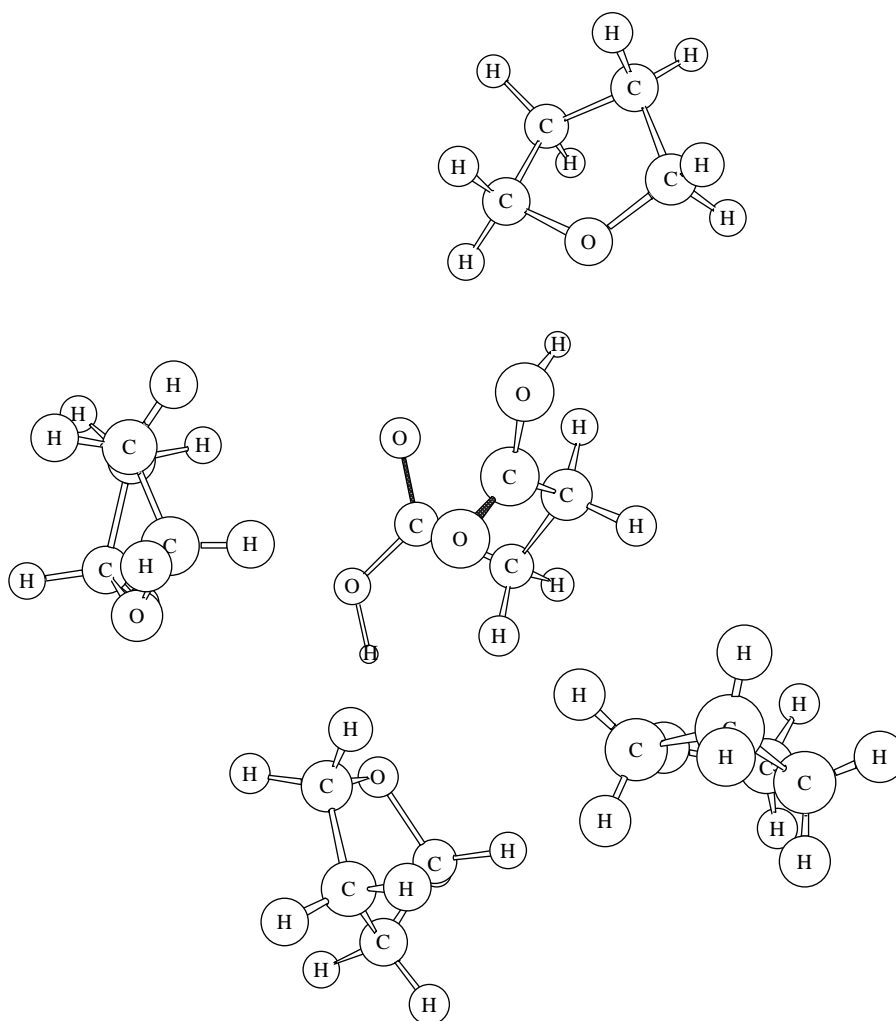


Figure 9. Optimised geometry of one molecule of succinic acid and four molecules of THF.

The relaxation time in water + THF binary system was seen to increase with the increase in the concentration of water. [13], a trend seen here for the τ_2 relaxation times.

From all the observations it is seen that τ_2 corresponds to the relaxation of THF alone, with a small influence

by the solute molecules. τ_1 in the case of SA and MA is seen to be much greater than the values obtained from solvation by 1-4D. τ_1 corresponds to the overall relaxation of the molecule and a large τ_1 value would normally imply the presence of a large agglomeration of molecules giving

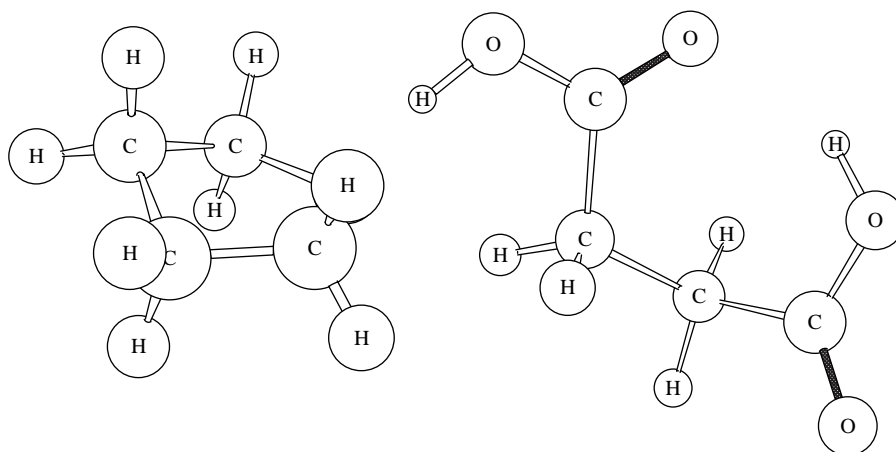


Figure 10. Optimised geometry of one molecule of succinic acid (trans) and one molecule of THF.

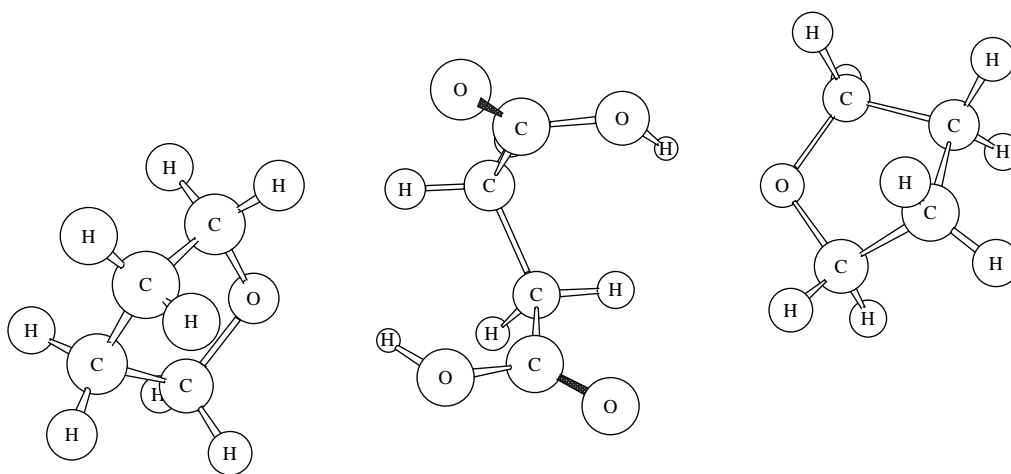


Figure 11. Optimised geometry of one molecule of succinic acid (trans) and two molecules of THF.

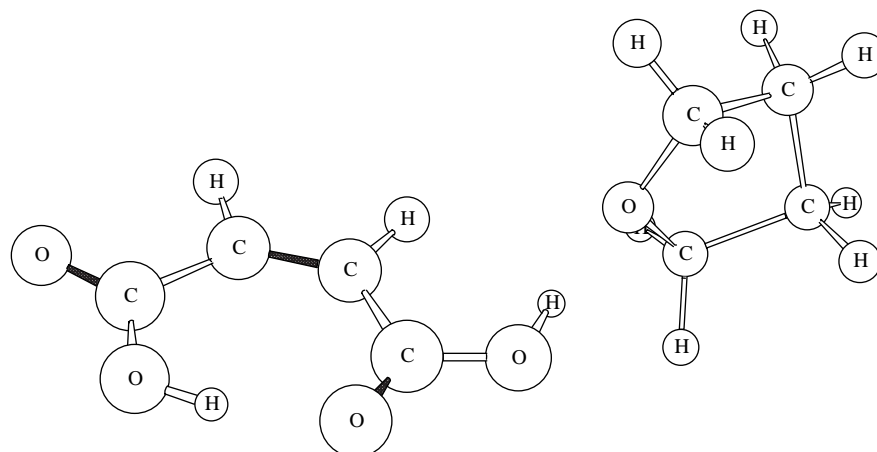


Figure 12. Optimised geometry of one molecule of maleic acid and one molecule of THF.

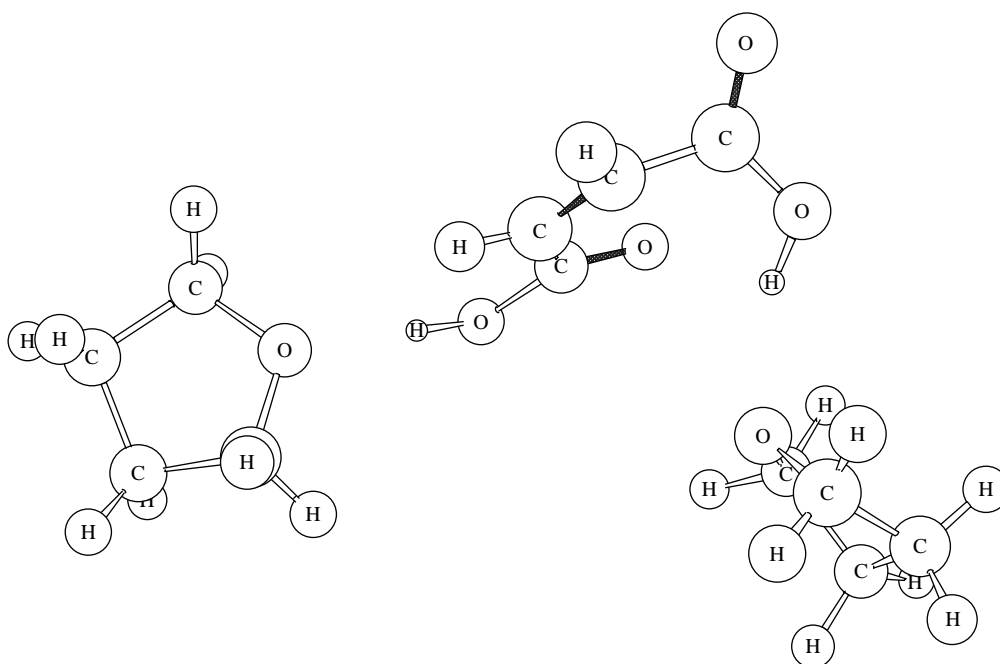


Figure 13. Optimised geometry of one molecule of maleic acid and two molecules of THF.

rise to a large relaxation time. The decrease of τ_1 with increasing solute concentration, in the present case could probably be due to the incomplete solvation of the solute molecules by the solvent. Hence the systems contain at least two distinct types of molecular motions, one due to the solvent molecules and the second due to the nano-clusters of the solute molecules.

It can be seen from the IR spectra that the hydrogen bonding in the solid state of SA is broken down on solvation by THF as seen from the sharp peaks in the 3200 cm^{-1} range. The splitting of the CO stretch peak at about 1670 cm^{-1} (of SA and THF) indicates the possibility of different conformations of the SA–THF interaction. Also this CO stretch peak undergoes a red shift to 1684 cm^{-1} in both SA and THF systems, further indicating the CO site as a site of hydrogen bonding. These interactions are taken into account while performing the conformational calculations for the SA–THF interactions.

4. Discussion

As seen from the data, there are two main features of the dielectric relaxation times and the dipole moment values of SA/MA in THF namely (i) that the intra and inter molecular interactions as indicated by τ_1 and τ_2 , are distinctly different and (ii) the dipole moment of SA/MA on solvation by THF is much smaller than that of either SA/MA or THF. These results are different from those of solvation of SA/MA by 1-4D, as reported previously by the authors. The data suggests an incomplete solvation of SA/MA by THF. This conclusion is further supported by earlier observations of the dielectric data of THF–water mixtures and solvation of SA by THF. It is assumed that the THF molecules are unable to completely break the intermolecular hydrogen bonding that exists in SA and hence are unable to complete the solvation. The present dielectric studies indicate that MA also undergoes similar effects on solvation by THF. An attempt has been made to resolve the experimental dipole moment of the SA/MA systems in THF by considering some specific solute–solvent interactions, but no clear resolution was possible. It is concluded that SA and MA exists as nano-sized clusters when solvated by THF.

The IR spectra of SA, THF and SA in THF are shown in figures 2–4. The shift in peak position is considerable but the peak shape does not have enough clarity to be resolved for the determination of the actual interactions. The shift in peak positions indicates the solvation of SA by THF and the subsequent breakdown of the intermolecular hydrogen bonds present in the solid state of SA and thus excludes the possibility of the presence of large clusters. But the dielectric data on the other hand suggest the presence of agglomerates of SA molecules in THF leading to two distinct relaxation times τ_1 and τ_2 .

Two relaxation times are associated with the relaxation of molecules in the liquid state. One relaxation time namely τ_1 corresponds to the overall relaxation of the

molecule that is, an end-to-end rotation of the system, and hence a longer relaxation time. The second relaxation time τ_2 corresponds to the shorter relaxation of the side-chains or segments of the molecule. Since this model corresponds to an ideal situation of two rotational motions, an average relaxation time, τ_0 , called the mean relaxation time is defined as $[\tau_1 \tau_2]^{0.5}$. The details of the relevant equations are the same as mentioned by Malathi *et al.* [8]. Different values of τ_1 and τ_2 due to the presence of larger backbone relaxation and shorter group relaxations have been previously reported in the case of some polymers [15]. Since in the present case two distinct relaxation times are seen, a similar phenomenon, namely the presence of a larger relaxation time due to a larger cluster consisting of a few molecules of SA and solvated by THF and the shorter relaxation time corresponding to the relaxation of THF are predicted.

It is thus seen that THF breaks down the large clusters of SA, but the solvation is incomplete, leading to the breakdown of large size particles of SA to nano sized clusters on solvation by THF. The presence of such clusters is inferred from the difference in the dielectric relaxation times τ_1 and τ_2 and also from the net dipole moment of the solute–solvent system, which is not attributable to any nominally small group of SA–THF molecules.

Since the dilute regime of the performance of the experiment excludes the possibility of the formation of large clusters, and is also the case as seen from the IR studies, but the dielectric relaxation data certainly indicate the formation of clusters, and also given the fact that THF is known to incompletely solvate SA in certain cases, it is concluded that nano-clusters of SA are formed when SA is solvated by THF. Since SA and MA show similar trends in their dielectric behaviour, it may be safely assumed that MA also shows similar behaviour on solvation by THF.

We further suggest the determination of dielectric relaxation times as a primary tool to investigate the incomplete solvation by simple solvents for non-polymeric molecules. The restriction on simple solvents and non-polymeric samples comes from the fact that the systems under study should themselves not have a large difference in τ_1 and τ_2 , which is taken to be an indication of incomplete solvation. Any conclusions regarding incomplete/complete solvation have to be backed by further studies on the dipole moments and conformational analysis, either experimentally or computationally, or even better, both.

5. Conclusions

The dielectric properties of SA and MA in THF were studied at microwave X-band frequency. The relaxation times of these systems determined using Higasi's method show a large difference between the overall and group relaxation times in both the systems. An attempt was made to determine the conformation of SA/MA and THF that would be closest to the experimentally determined dipole

moment, but no simple structure was found. Taking all these observations along with the IR data into consideration, it is inferred that THF solvates SA/MA, but incompletely, thus leaving behind nano-clusters of SA/MA. These clusters relax with a characteristic time that is larger than that of the smaller THF molecule, thus giving rise to two distinct relaxation times. The experimentally observed dipole moment is taken to be the average over (i) molecules in a cluster and (ii) over many clusters in the bulk of the liquid. We further suggest the determination of relaxation times as a preliminary tool for the study of incomplete solvation of simple molecules.

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