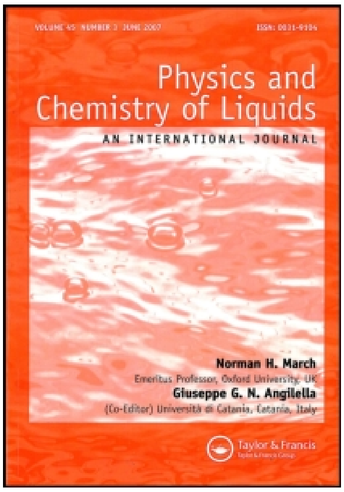

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V. Madhurima[a]; B. Viswanathan[b]; V. R. K. Murthy[a]
[a] Department of Physics, Indian Institute of Technology - Madras, Chennai, India 600 036 [b] Department of Chemistry, Indian Institute of Technology - Madras, Chennai, India 600 036

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Effect of steric hindrance of ketones in the dielectric relaxation of methanol + ketone systems

V. MADHURIMA*†§, B. VISWANATHAN‡ and V. R. K. MURTHY†

†Department of Physics, Indian Institute of Technology – Madras, Chennai, India 600 036
‡Department of Chemistry, Indian Institute of Technology – Madras, Chennai, India 600 036

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The reorientation activation energies of five methanol + ketone systems were determined from the study of the variation of dielectric permittivity with temperature between 303 to 333 K at X band frequency. The results of the activation parameters are interpreted in terms of the rotation of the molecules about the C–O–H hydrogen bond, using a previously reported conformation obtained from semi-empirical and *ab initio* calculations as the basic conformer. The ketones studied are acetone, 2 butanone, 3 pentanone, cyclohexanone and acetophenone.

Keywords: Dielectric; Steric hindrance; Ketones; Methanol

1. Introduction

There have been few studies in the past on the effect of steric hindrance of molecules on their dielectric properties. The number and nature of hydrogen bonds in super cooled water and alcohols was found to depend on the nature of steric hindrance offered by the molecules to the OH group [1]. The effect of packing of n-butane on its conformation has been reported by Pratt *et al.* [2].

The study of liquid state and the interactions therein requires a comparative study involving more than one technique. Dielectric permittivity data by themselves cannot predict the actual sites of interactions in binary systems. The rotational activation energies that are determined from microwave dielectric studies give values of entropy far exceeding values that can be explained in terms of translation, rotation and vibrational entropies. Hence only a relative comparison of the entropy value for the different members of a homologous series is useful. Since the actual site of interaction cannot be predicted from dielectric studies, such a conformation is obtained from semi-empirical and *ab initio* computational studies.

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*Corresponding author V. Madhurima. Email: vmsp@uohyd.ernet.in
§Present address: School of Physics, University of Hyderabad, Hyderabad 500 046, India.

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The reorientational thermodynamic parameters were determined using Eyring's equation [3] and the dielectric relaxation time τ was calculated from Gopalakrishna method [4]. The plot of $\ln(\tau T)$ versus $(1/T)$ is, where T is the temperature of measurement, is found to be linear. From this plot the energy parameters are derived. Since the plot of $\ln(\tau T)$ versus $(1/T)$ is linear, the systems either have a single relaxation time or the difference between the relaxation times at this frequency is too small to differentiate [5].

The original equation of Eyring was to explain the chemical reaction of the form $A + B \leftrightarrow C$. This was later modified to explain the dipole reorientation process. This is essentially a "borrowed" model and hence no significance is attached to the absolute values of entropy (ΔS) determined. Only the sign and the relative magnitude of ΔS in a homologous series are considered. Hence only the sign and the relative values are appropriate for understanding the rotational mechanism.

In order to overcome these inherent difficulties in the present study, the conformation of the first system is determined from elaborate computational studies, and using this conformation as reference the hydrogen bonding sites for the other homologues is assigned. The activation thermodynamic parameters are interpreted in terms of rotation of the molecules about the C–O–H hydrogen bond.

2. Experimental details

All samples were of Analar grade with purity greater than 99% and were distilled before use and stored over 4 Å molecular sieves. The non-polar solvent used for dielectric studies was benzene. The five systems of choice for the present study are methanol+acetone, 2 butanone, 3 pentanone, cyclohexanone and acetophenone. Dielectric permittivity studies for relaxation time measurements were performed using flat movable plunger technique at 9.70 GHz (X Band). The least square fit for the reflected power profile with 100 or more data points was obtained by optimising the values of attenuation constant, propagation constant and the saturation power output. All experiments were performed at room temperature (300 K).

Ketones have the general formula R–CO–R′ where R and R′ are alkyl groups that may or may not be identical. The ketones chosen for the present study are methanol + acetone, 2 butanone, 3 pentanone, cyclohexanone and acetophenone. Acetone is the first homologue of the ketones. The chain length increases as one goes from acetone to pentanone. Cyclohexanone with six carbons has one carbon more than 3 pentanone but has a ring like structure. This fact is made use to understand whether the reorientation process is due to the actual number of carbon atoms or due to steric hindrance. Sterically acetophenone is similar to acetone with respect to the hydrogen bond although the number of carbon atoms in acetophenone is eight in comparison to the three in acetone. Both the systems have CH_3 group next to the hydrogen bond site. Acetone has two CH_3 groups whereas acetophenone has one.

In the study of hydrogen bonds in the binary systems of carbonyl compounds with OH groups, the angle of the bond is generally taken to be along the sp^2 lone pair. Thus the angle between the OH axis and the carbonyl group is taken to be 60° [6].

3. Results and discussion

The values of the relaxation time τ, reorientation activation free energy (ΔF), reorientation activation enthalpy (ΔH) and the reorientation activation entropy (ΔS) for the five binary systems are given in table 1. ΔF is seen to be constant in the given temperature region. From the data it is seen that the ΔS values are all negative, which indicate that the binary system is in a stable conformation even without the application of an external field. On the application of an external field (the microwaves here) the binary system takes on a conformation that has a higher energy than the ground state. Larger entropy value (magnitude wise) means that the system is more stable and hence possess more freedom. Lowering of the entropy value implies that the system is being "frozen". In the case of dipole reorientation "frozen" would mean a hindered rotation. Any given system can have a number of conformations of which the most probable conformation has minimum steric hindrance (hindrance due to the proximity of two or more atoms or molecules).

The two possible conformations of the acetone–methanol system are shown in figure 1 [7]. The possible conformation of the acetone and methanol system was

Table 1. Dieletric relaxation time and thermodynamic parameters for methanol + ketone systems.

System Methanol+	Temperature (K)	τ (ps)	ΔH (kcal mol^{-1})	ΔF (kcal mol^{-1})	ΔS (kcal mol^{-1})
Acetone	299	11.08	1.19	2.52	−4.44
	308	10.18		2.56	−4.45
	313	9.68		2.58	−4.44
	318	9.25		2.60	−4.44
	323	8.85		2.62	−4.44
2 Butanone	303	9.11	1.74	2.43	−2.26
	308	8.97			
	313	8.80		2.52	−2.25
	318	8.74		2.57	−2.60
	323	8.67		2.61	−2.70
	328	7.22		2.54	−2.45
	333	6.05		2.47	−2.21
3 Pentanone	303	17.20	2.07	2.82	−2.49
	308	15.19		2.80	−2.39
	313	14.04		2.81	−2.37
	318	13.47		2.84	−2.43
	323	12.54		2.85	−2.42
	328	11.82		2.86	−2.43
	333	11.29		2.89	−2.46
Cyclohexanone	303	16.58	1.16	2.80	−5.41
	308	15.81		2.83	−5.41
	313	15.00		2.85	−5.39
	318	14.54		2.89	−2.42
	323	13.80		2.90	−5.41
	328	13.22		2.94	−5.41
	333	12.65		2.96	−5.40
Acetophenone	303	16.38	1.36	2.76	−4.62
	308	15.64		2.78	−4.47
	313	15.43		2.70	−4.21
	318	13.42		2.72	−4.21
	323	13.35		2.71	−4.12
	328	13.27		2.67	−3.94
	333	12.19			

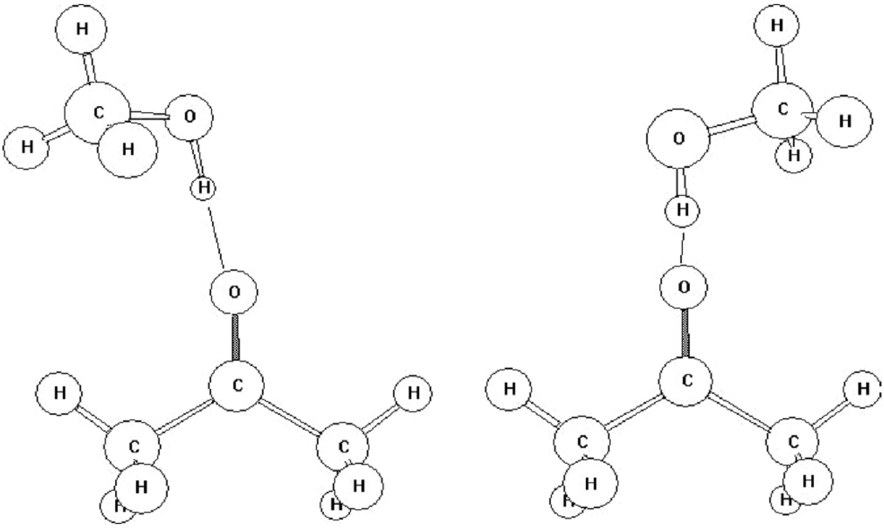

Figure 1. Two possible conformations of methanol–acetone interaction, as determined from *ab initio* calculations.

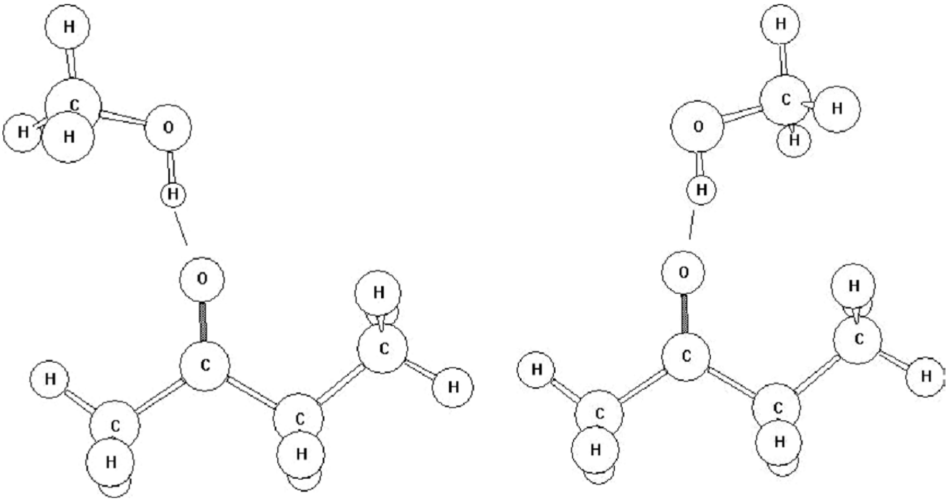

Figure 2. Two possible conformations of methanol–2 butanone interactions, with the rotation about the hydrogen bond being implied.

determined from semi-empirical and *ab initio* Hartree–Fock calculations and this is taken to be the basic structure for the present studies. The two orientations exist because the methanol molecule is free to rotate about the O–H–O bond. As the chain length of the ketone molecule increases, i.e. as one goes from acetone to 2 butanone, the methanol molecule sees an additional hindrance to rotation in one of the directions (figure 2) in the form of an additional CH_2 group to one side. Due to this hindrance, the methanol molecule has a preferred orientation (towards the side without the CH_2 group), and hence gets "frozen" in that state. This accounts for the lowering of entropy of the 2 butanone + methanol system compared to the acetone + methanol system.

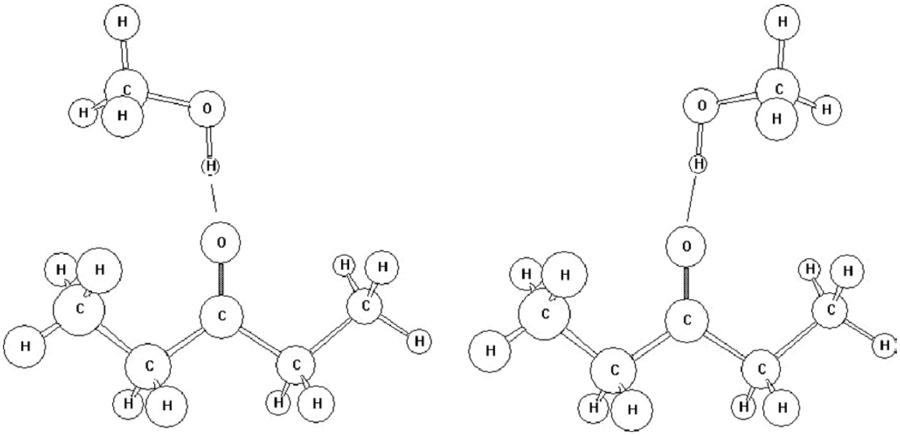

Figure 3. Two possible conformations of methanol–3 pentanone. The symmetry of the system indicates the equal probability of both the interactions.

A further reduction of entropy is seen for the 3 pentanone+methanol system since the methanol molecule is subjected to hindrance as compared to acetone or 2 butanone, on both sides of the O–H–O bond as seen from figure 3.

On going from the 3 pentanone, which is a linear ketone, to cyclohexanone, which has a closed ring like conformation, an increase in the entropy value is seen. ΔS value of the cyclohexanone + methanol system is grater than that of acetone + methanol system. This is because in the cyclohexanone + methanol system the methanol molecule "sees" no hindrance to its rotation on either side of the O–H–O bond, in comparison to the CH_3 hindrance encountered in the acetone + methanol system (figure 4).

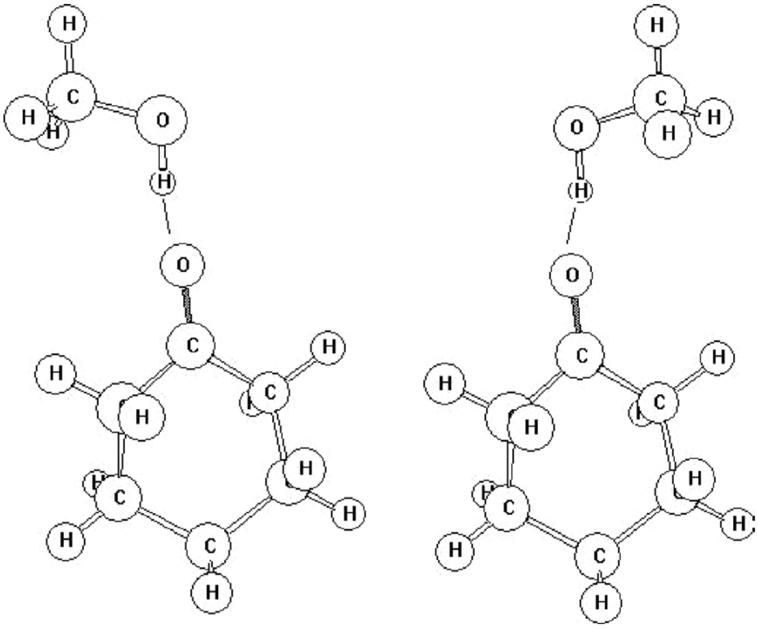

Figure 4. Two possible conformations of methanol–cyclohexanone. A greater degree of rotational freedom is seen about the hydrogen bond.

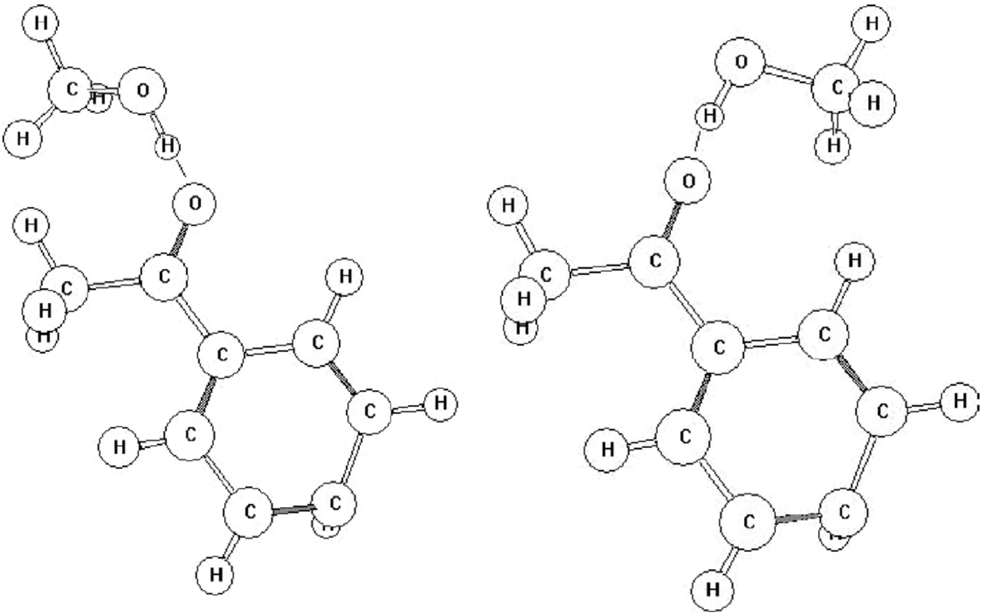

Figure 5. Two possible conformations of methanol–acetophenone. Steric hindrance to the rotation of the methanol molecule about the hydrogen bond is possible due to the presence of the methyl group of acetophenone.

The ΔS value of the acetophenone + methanol system is intermediate to the values of acetone + methanol system and cyclohexanone + methanol system. This is attributed to the fact that acetophenone has a CH_3 group to one side of the O–H–O bond (figure 5) compared to the two of acetone and none of cyclohexanone systems.

From the ΔS values it is seen that the steric hindrance rather than the actual number of carbon atoms in the ketone molecule plays an important role in the reorientation process of the methanol molecule in the ketone + methanol systems.

4. Conclusions

Dielectric permittivity data often yields only a qualitative model of the reorientation mechanism in liquids. In the present study the dielectric permittivity data was used to determine the reorientation thermodynamic parameters. The results of these studies are compared with pre-determined structures of ketone + methanol system and the actual mechanism of dipolar reorientation is studied. It is found that the actual number of carbon atoms in a homologous series is not important. The conformation of these molecules and hence the steric hindrance presented by them is the determining factor for the reorientation. It is also seen that a combined scrutiny of dielectric and conformational analysis data can yield much more information about the rotational dynamics of the systems when compared to dielectric data alone.

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