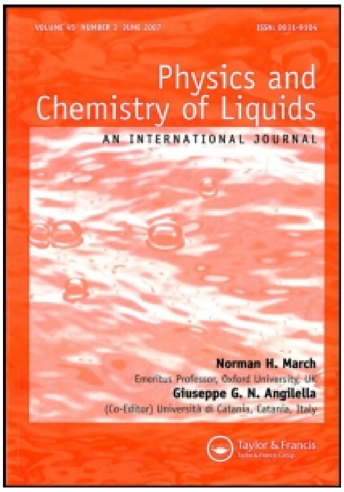

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Dielectric Relaxation in OH—O Bond Complexes

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The dielectric absorption of the mixtures of Phenol with Acetone and Ethyl methyl ketone having different concentration ratios (3:1, 2:1, 1:1, 1:2 and 1:3) has been determined at microwave frequency 9.8 GHz, at 33°C. The dielectric data have been analyzed, to yield relaxation times and dipole moments, using Higasi method and Higasi, Koga and Nakamura method. All the mixtures yielded high values of the distribution parameter indicating the flexible nature of the OH—O type hydrogen bonding. The high values of the relaxation times and dipole moments give confirmative results for the association of the phenol with these electron donar molecules in all mixtures investigated.

INTRODUCTION

For the study of complex formation through hydrogen bonding, the most commonly used technique is either I.R. or U.V. spectroscopy. The first of these methods can not normally be used for solutions in hydrocarbons but only in solvents such as carbon-tetrachloride, where as for the second the reverse applies. The cross checking of results through these methods is therefore limited. The study of the complex formation based on dielectric constant measurements has been found to be more accurate and suitable by many workers.[1–3] It can be applied to solutions in any non-polar solvents. In addition the electric dipole moment of the complex can also be obtained. This method provides information about the stereochemistry of the complex and the electronic perturbations there in. In their study Magee and Walker[4] suggested that the investigation of relaxation time, distribution parameter, and dipole moment provides the most effective measure to study the problem

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of complex formation. Recently Saxena *et al.*[5] have studied the OH—N bond complexes of (Pyridine + Phenol) and (Quinoline + Phenol) systems by utilizing the dielectric method. The strongly hydrogen bonded (NH—N) complexes have been studied by Gupta *et al.*[6]

The OH—O bond complexes have been most commonly studied using infra-red techniques.[7,8] Widom *et al.*[9] have studied the association of Phenol with several Ketones using i.r. absorption measurements. They have calculated the equilibrium constant for the dissociation of carbon-tetrachloride solutions of hydrogen bonded complexes between phenol and ketones. Due to limited dielectric investigations on OH—O bond complexes, it was considered worthwhile to undertake a dielectric study of complex formation of Acetone and Ethyl methyl Ketone with Phenol of different concentration ratio in carbon-tetrachloride. In the present study the single frequency concentration variation method of Higasi[10] has been applied to evaluate the relaxation parameter of dipolar rotation and distribution parameter. The values of distribution parameter are sufficiently high indicating more than one relaxation process present in the system. The dielectric dispersion has therefore been further resolved using Higasi, Koga and Nakamura method[11] in terms of $\tau_{(1)}$ and $\tau_{(2)}$ corresponding to the relaxation time of one complex species and to the molecular relaxation time of the whole complex molecule respectively. The dipole moments of the complexes of different concentration ratios have been evaluated using Higasi method.[12] The increase in dipole moment of the complex has been discussed in terms of the bending of OH—O bond towards phenol due to the repulsive force of the alkyl group of Ketone.

THEORY

The most probable relaxation time $\tau_{(OH)}$ and the distribution parameter (α) associated with the complex species have been evaluated by Higasi method[10] using Eq. (1) and (2)

$$\tau_{OH} = \frac{1}{\omega} \cdot \left(\frac{A^2 + B^2}{C^2}\right) \frac{1}{2(1 - \alpha)} \tag{1}$$

$$1 - \alpha = \frac{2}{\pi} \cdot \tan^{-1} \cdot \frac{A}{B} \tag{2}$$

where A, B and C parameters have their usual meanings.

Since the values of the distribution parameter (α) have been found to be sufficiently high for all solute concentrations, the dielectric dispersion has been further resolved by Higasi *et al.* method.[11] $\tau_{(1)}$ corresponds to the relaxation time of the flexible part of the complex and $\tau_{(2)}$ corresponds to the molecular relaxation time of the complex formed as a whole due to the association of Phenol and Acetone and Ethyl methyl Ketone. The values of $\tau_{(1)}$ and $\tau_{(2)}$ have been evaluated using (3) and (4)

$$\tau_{(1)} = \frac{1}{\omega} \cdot \frac{a''}{(a' - a_\infty)} \tag{3}$$

$$\tau_{(2)} = \frac{1}{\omega} \cdot \frac{a_0 - a_\infty}{a''} \tag{4}$$

The apparent dipole moment of the complex has been computed using Eq. (6) given by Higasi[12]

$$\mu_{ab}^2 = \frac{27KT}{4\pi N} \cdot \frac{M_2}{d_1} \cdot \frac{(a_0 - a_\infty)}{(\varepsilon_1' + 2)} \tag{5}$$

$$= B^2(a_0 - a_\infty)$$

$$B = \left\{\frac{27KT\,M_2}{4\pi N d_1}\right\}^{1/2} \cdot \frac{1}{(\varepsilon_1' + 2)}$$

The terms ε_1' and d_1 represent the dielectric constant and the density of the solvent, M_2, is the molecular weight of the complex the other symbols have their usual meanings. The change in the dipole moment $\Delta\mu$ has been calculated using Eq. (6)

$$\Delta\mu = \mu_{ab} - \mu_a - \mu_b \tag{6}$$

where μ_{ab} is the dipole moment of the complex and μ_a and μ_b are the dipole moments of phenol and base molecules respectively.

EXPERIMENTAL DETAILS

The chemicals Phenol, Acetone and Ethyl methyl Ketone have been obtained from BDH England. The physical properties of the chemicals were checked against their literature values. The solvent carbon-tetrachloride used in the measurement was distilled twice before use.

The methods of evaluating the dielectric parameters have been given in our earlier papers.[5,13,14]

RESULTS AND DISCUSSION

The values of the slopes a_0, a', a'' and a_∞ for all the samples in dilute solution of carbon-tetrachloride are reported in Table I. Table II contains the values of the distribution parameter, the relaxation times calculated by Higasi and Higasi *et al.* method, and the dipole moments.

TABLE I

Slopes a_0, a', a'' and a_∞ for different proportions of the component in CCl_4 at 33°C.

Solute concentration	a_0	a'	a''	a_∞
Acetone + Phenol				
3:1	20.00	7.69	5.3	0.04
2:1	22.22	8.33	5.0	−0.06
1:1	18.18	6.25	4.7	+0.77
1:2	20.00	6.67	4.0	0.05
1:3	16.00	7.00	6.0	0.11
E.M.K. + Phenol				
3:1	17.14	—	—	0.08
2:1	21.15	7.2	4.2	0.06
1:1	20.8	6.9	4.0	0.05
1:2	18.9	6.1	3.5	−0.11
1:3	16.0	5.2	3.2	0.05
Acetone	30	—	—	−0.20
EMK	20	—	—	−0.12

TABLE II

Relaxation times, distribution parameters and dipole moments values

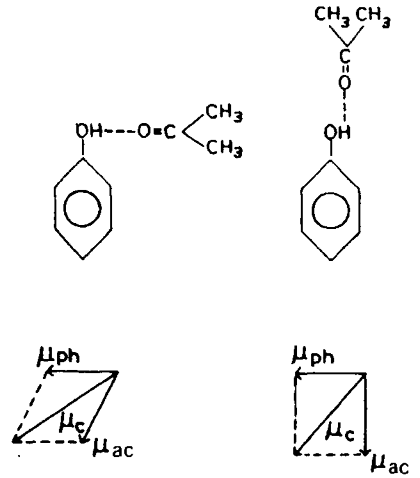
	Higasi, method		Higasi, Koga Nakamura method			
Solute concentration	τ_{OH} ps	α	$\tau_{(1)}$ ps	$\tau_{(2)}$ ps	Dipole-moment $\mu_{ab}(D)$	$\Delta\mu$ D
Acetone + Phenol						
3:1	28.9	0.36	11.3	37.7	4.18	−0.52
2:1	34.1	0.44	9.7	45.1	4.41	−0.29
1:1	45.3	0.40	11.8	48.8	3.91	−0.79
1:2	49.6	0.47	9.8	54.1	4.18	−0.52
1:3	23.4	0.41	9.7	36.5	3.74	−0.96
EMK + Phenol						
3:1	—	—	—	—	3.69	−0.74
2:1	48.2	0.48	9.6	53.9	4.14	−0.29
1:1	52.8	0.49	9.5	56.4	4.08	−0.35
1:2	59.2	0.50	9.5	59.4	3.59	−0.84
1:3	52.3	0.47	9.2	54.8	3.62	−0.81
Phenol	8.9(5)	0.45	—	—	1.77(5)	
Acetone	3.2	—	—	—	3.0	
E.M.K.	—	—	—	—	2.73	

DISCUSSION

Acetone + Phenol

The most probable relaxation time for 1:1 mixture is found to be 45.3 ps, which is much longer than the relaxation times of Acetone (3.2 ps) and of Phenol (8.9 ps). The relaxation time of the mixture is significantly longer than those of the components suggesting the association of the two molecules by hydrogen bond of OH—O type. The length of the relaxation time depends on the shape and size of the associating compounds. The distribution parameter has been found to be 0.40 which is sufficiently high. The high value of α indicates the weaker and flexible nature of the hydrogen bond. This is most probably due to the smaller electron donating power of Acetone and the flexible nature of Phenol. Due to the high value of α the dielectric data has been further resolved in terms of $\tau_{(1)}$ and $\tau_{(2)}$ using Higasi *et al.* method.[11] As may be seen from the Table II that $\tau_{(2)}$ (48.8 ps) is much longer than the $\tau_{(1)}$ (11.8 ps), it was considered that the $\tau_{(1)}$ corresponds to the relaxation time of one complex species suggested by Magee *et al.*[15] The $\tau_{(1)}$ values are very close to relaxation time of Phenol and vary irregulary from 11.8 ps to 9.7 ps for all the five mixture ratios. The $\tau_{(2)}$ value (48.8 ps), for 1:1 mixture compares well with the τ_{OH} value (45.3 ps), showing the relaxation time of the complex molecule. The $\tau_{(2)}$ and τ_{OH} both increase on increasing the amount of phenol and are reduced with the increasing amount of Acetone. The increase of the relaxation time with the increasing amount of phenol indicates that the excess amount of Proton donar molecules produces more hinderence in the solution. The $\tau_{(2)}$ and τ_{OH} both decrease rapidly for 1:3 mixture which most probably represent the average relaxation time of 1:1 complex and unassociated phenol. These results are consistent with our earlier study[5] of OH—N bond complexes (Pyridine + Phenol, Quinoline + Phenol) and with the observation of Frost and Smyth,[16] that the relaxation time of a binary mixture depends upon the concentration ratio as well as on the nature of the components.

The dipole moments of all the five mixtures have been evaluated using Higasi method.[12] These are found to be greater than the dipole moments of the components. So it again gives the confirmative results for the association of Acetone and Phenol in all the five different concentration ratios selected for the measurements. The formation of hydrogen bond produces the displacement of the electrons and nuclei which results in a difference between the dipole moment of the complex and the scalar sum of the individual moments of the components. This difference ($\Delta\mu$) may be positive or negative, when one or both of the components are polar as suggested by Sahney *et al.*[17] In the present study $\Delta\mu$ has been found to be negative for all different concentration ratios. The most probable explanation for the negative value of



(a) Linear position (b) Bent position

FIGURE 1

$\Delta\mu$ is that the repulsion between the alkyl groups of ketones causes the axis of ketone to incline towards that of the phenol group and so to bend the OH—O system which otherwise would be linear (see Figure 1). This would cause the angle between phenol moment and Ketone moment to increase and possibly even to become obtuse and so would reduce the moment of the complex to less than the scalar sum of the moments of the two components. Similar conclusion has been drawn in the Triphenyl methonal + Phenol complex by Hulett *et al.*[18] The alternative explanation for the negative value of $\Delta\mu$ is the low value of association constant ($=8$) and less solubility of the complex as observed by the i.r. study.[9]

Ethyl methyl Ketone + Phenol

As may be seen from Table II, that the sufficient high values of the distribution parameter for all the different concentration ratios taken for measurements again indicate that the interaction of these molecules is weak as has been found in the mixture of Phenol and Acetone. The most probable relaxation time τ_{OH} for 1:1 mixture has been found to 52.8 ps which is greater than the corresponding relaxation time (45.3 ps) for Acetone: Phenol mixture. The increase in the relaxation time is a direct consequence of greater molecular volume as given by the simple theory

$$\tau = \frac{3\eta V}{kT}$$

where V is the molecular volume and η, the macroscopic viscosity. Here EMK : Phenol complex molecule is more bulky than that of Acetone : Phenol. The variation of the relaxation time with concentration ratio is the same as has been found for the acetone : Phenol system. The $\tau_{(1)}$ values are more close to the relaxation time of phenol molecule and $\tau_{(2)}$ and τ_{OH} values are very much near to each other as has been found for the previous system. The apparent dipole moment of the complex as has been found to be greater than the dipole moments of components indicating the association of these molecules. The negative value of $\Delta\mu$ may be explained in the way similar to that adopted for the Acetone + Phenol system.

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