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Dielectric relaxation of non-rigid polar molecules and their mixtures in 1:4 dioxane

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The dielectric constant and loss factor of the non-rigid polar molecules of *o*-chloronitrobenzene (I) and 2-chloro-5-aminobenzotrifluoride (II) and their binary mixtures have been measured in dilute solutions of 1:4 dioxane at 9.93 GHz over the temperature range 25–55°C. The dielectric data have been used to determine the relaxation times and thermodynamic parameters for the activated state. The relaxation behaviour of the mixtures is found to be the resultant of the relaxation times of its components, suggesting a simple overlap of the individual dispersion regions. The relaxation times of the mixtures have also been obtained and compared with the values computed using various theoretical formulations. The results indicate that none of the formulae used can predict the experimental results to a satisfactory degree.

THE dielectric relaxation behaviour of binary polar mixtures, as suggested by Schallamach¹, and other workers^{2,3}, in which both the components are either associated or non-associated, is much different from that of mixtures in which one component is associated and the other non-associated. Besides, dielectric absorption studies have indicated that the relaxation behaviour of polar molecules depends not only on their own interactions but also on their characteristic interaction with the solvent molecules. It therefore seems worthwhile to examine the dielectric relaxation of mixtures of two different polar compounds in a solvent like 1:4 dioxane, which shows hydrogen bonding with various anilines^{4,5}. The present study deals with the relaxation behaviour of mixtures of *o*-chloronitrobenzene (I) and 2-chloro-5-aminobenzotrifluoride (II) with various compositions in 1:4 dioxane at temperatures in the range 25–55°C. Both compounds are non-rigid and polar; I is non-associative and II is weakly associative in

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character. There exists a finite possibility of hydrogen bonding between II and 1:4 dioxane.

The relaxation time (τ_0) has been determined following the method of Higasi⁶, using the experimental technique of Heston *et al.*⁷ The thermodynamic parameters have been calculated using Eyring's⁸ theory of rate process. Compounds I and II (Fluka) were used as supplied; 1:4 dioxane (AR grade) was purified by the usual methods.

The values of most probable relaxation time τ_0 listed in Table 1 for three compositions of the mixture and at four temperatures lie between those of the individual components, but vary with the concentration ratio of the components. For resolution of two distinct relaxation processes Davidson⁹ suggested that the relaxation time of one component should be 5.8 times that of the other. However, in the present case, the ratio of most probable relaxation times of I and II is much less than 6, thus separate loss maxima are not likely to appear. Thus apparent single relaxation time can be assumed to represent the true behaviour of the mixture systems. The τ_0 value is found to increase with increase in mole fraction of II but the gradient of increase is not linear. As the mole fraction of II increases beyond 0.44 a sharp increase in τ_0 is observed. This increase is evident from the structure of II, where the presence of $-\text{NH}_2$ group facilitates hydrogen bonding between hydrogen of $-\text{NH}_2$ group and oxygen of 1:4 dioxane, such that, with an increase in the mole fraction of II in the mixture, the association between solute and solvent increases. Studies of microwave absorption by Deogaonkar *et al.*^{10,11} indicated formation of complexes through hydrogen bonding in some binary liquid mixtures of chlorophenol with various compounds like toluidine, anilines, etc. They observed a prominent maximum in the $\tan\delta$ -concentration curve for these compounds and attributed the results to an association between the two types of molecules. However, in the present case, the $\tan\delta$ -concentration curves are more or less linear at all temperatures. Thus the relaxation behaviour of each mixture studied here is the resultant of the relaxation times of its components, suggesting a

Table I. Relaxation times determined (τ_0) and calculated (τ_{mix}), and thermodynamic parameters of *o*-chloronitrobenzene (I) and 2-chloro-5-aminobenzotrifluoride (II) and their mixtures in 1:4 dioxane.

Mole fraction of II in mixture (I + II)	Temp (K)	Relaxation time ($\times 10^{12}$ sec)				ΔF_e (kcal mol ⁻¹)	ΔH_e (kcal mol ⁻¹)	ΔS_e (cal mol ⁻¹)
		τ_0	τ_{mix} (a)	τ_{mix} (b)	τ_{mix} (c)			
0.00	298	58.4	—	—	—	3.49	5.95	8.26
	308	40.2	—	—	—	3.40	5.95	8.28
	318	29.9	—	—	—	3.34	5.95	8.21
	328	21.2	—	—	—	3.24	5.95	8.26
0.20	298	72.4	80.6	67.2	75.0	3.62	5.35	5.81
	308	52.1	59.7	46.8	53.3	3.56	5.35	5.81
	318	40.9	43.1	34.7	39.5	3.54	5.35	5.69
	328	28.2	33.3	24.9	28.8	3.43	5.35	5.85
0.44	298	79.3	107.2	82.0	96.7	3.67	4.76	3.66
	308	60.6	83.1	58.4	71.3	3.65	4.76	3.60
	318	48.4	59.0	42.9	52.2	3.65	4.76	3.49
	328	35.4	47.9	31.5	39.4	3.58	4.76	3.60
0.71	298	95.9	137.1	109.1	126.3	3.78	3.75	-0.10
	308	93.5	109.5	80.9	97.1	3.91	3.75	-0.52
	318	77.7	76.9	58.5	69.9	3.95	3.75	-0.63
	328	60.3	64.3	44.7	55.3	3.92	3.75	-0.52
1.00	298	169.2	—	—	—	4.12	4.10	-0.07
	308	137.8	—	—	—	4.15	4.10	-0.16
	318	96.1	—	—	—	4.08	4.10	0.06
	328	81.9	—	—	—	4.12	4.10	-0.06

(a) and (b), ref. 14, (c), ref. 15.

simple overlap of individual dispersion regions. The degree of overlap, however, varies with the concentration ratio of the individual components in the mixture. The values of τ_0 decrease systematically with increase in temperature for the pure components as well as the mixture systems. Moreover, the values of τ_0 at nearly 50% composition of each component in the mixture are always lower than the mean of τ_0 values of the individual components for all temperatures. However, this difference shows some variation with temperature. This suggests that, although the mixture behaves like a superposition of individual relaxation behaviours of the components, the degree of superposition changes with temperature. These results are in agreement with the relaxation behaviour of some other polar mixtures^{12,13}.

A quantitative study of the thermodynamic parameters indicates that the values of free energy of activation (ΔF_e) are higher for II compared to those of I. Likewise, the values of ΔF_e are found to increase with increase in mole fraction of the former component in each mixture system. This confirms that the property of hydrogen bonding and solute-solvent interactions are truly maintained in the mixture systems. Further, the values of entropy ΔS_e for component I are positive and distinctly higher than those of component II, which are negative. However, ΔS_e values for the mixtures are generally intermediate between the values for the individual components, with the exception of the mixture consisting of 0.71 mole fraction of II, which has the most negative ΔS_e values. This suggests that a mixture composition due to possible interactions between the

two polar solute molecules may even be more ordered than the pure component with the most ordered state.

The different methods used for predicting the relaxation time of mixtures (τ_{mix}) have been employed earlier¹⁴. The overall absolute percentage deviations for the values computed by simple mixing rule (a), reciprocal mixing rule (b) and by Madan's¹⁵ method (c) are respectively 29.8, 8.1 and 19.1 at 25°C; 22.9, 9.1 and 8.0 at 35°C; 9.4, 17.1 and 7.1 at 45°C; 20.0, 16.2 and 7.2 at 55°C (Table I). Hence the τ_{mix} values computed for the present systems cannot be predicted successfully by any of the three methods used. Although, in the present case, the assumptions made by Madan¹⁵ are not fully met in these mixtures, Madan's¹⁵ method shows a relatively better agreement with the experimental values. This may probably be explained by the role of dioxane molecules, which interact strongly with system II through hydrogen bonding. Thus, if various other parameters involved in the rotation of polar molecules are included in computing the values of τ_{mix} , the relation by Madan can be expected to give better agreement with the experimental results for the systems investigated in the present study.

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Mycorrhiza: A possible deterrent in artificial cultivation of morels

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We report, for the first time, four species of morels that are in mycorrhizal association with the roots of some herbaceous plants in the northwestern Himalayas. It appears that the perhaps obligate mycorrhizal association of these morels may be responsible for the failure of earlier attempts to cultivate them artificially.

MORELS are a cherished delicacy and an important minor forest produce, with enormous economic potential, presently being sold at Rs 2200–2500 per kg in the Indian market¹. Various attempts have been made to domesticate this natural commodity since very early times but with little success². The indoor artificial cultivation of mushrooms has been successfully achieved in about fifteen species the world over³. This has, however, been possible only in the case of non-mycorrhizal mushrooms, where a successful imitation of natural processes has been possible.

The morels were not known to enter into any mycorrhizal relationship till we briefly reported this association in *Morchella esculenta*⁴. Later a similar but more detailed and definitive relationship between *M. rotunda* (Pers.) Boudier and some living trees and herbaceous plants was described and discussed by Buscot and Roux⁵. In the meantime we observed other morel species to enter into mycorrhizal relationship. The observations on the same relationship are being presented here.

Mycorrhizal connections were established by digging the soil and tracing the roots of the plant species to the fructifications following Young^{6,7}, and Zak^{8,9}. The

roots of plants associated were thoroughly washed with tap-water, and after fixing them in FAA for 24 h they were preserved in 70% alcohol. In order to confirm the formation of mycorrhizae, both stained (cotton blue in Lactophenol) and unstained sections were prepared and examined microscopically.

Observations for mycorrhizal association between the sporocarps of *Morchella deliciosa*, *M. esculenta* and *M. conica* and the roots of strawberry, grasses and fern rhizomes were made visually. The sporocarps were taken out carefully along with some mass of soil. These were allowed to dry and then freed from soil particles or they were washed slowly in running water to remove the dirt. The subterranean portion of the carpophore was seen to form a loosely woven cord near its base, which was gradually transformed into a more compact and shapely cord, producing some short roots on way, and tapering at the distal end and there getting connected to the farther end of the roots of these plants, forming a 'mycorrhizal bridge' (Figure 1, a–f; Figure 2, a–c).

Anatomical observations made on sections stained with cotton blue, show that morel hyphae penetrate into all the tissues of roots except xylem (Figure 2, d). The hyphae penetrate into the cells where they mostly grow near the cell wall but they also sometimes grow more deeply within the lumen. The root hairs are mostly absent. The typical fungus mantle was also absent. The hyphae have not been seen to grow intercellularly. In longisections of the root, the hyphae were seen to form a loose web on the root periphery; some of them penetrating directly into the cell lumens (Figure 2, e). The short roots also show a similar structure and they are almost evenly distributed all along the long root and its branches.

As has been observed in the present investigations, Buscot and Roux⁵, also had noted that ascocarps of *Morchella rotunda* are joined by subterranean hyphal systems, the 'mycelial muffs', surrounding living roots of various plants. Anatomically, the fungus has been found to penetrate almost all cells lying outside the xylem. They noted that from the 'mycelial muffs' the fungus penetrates into the root tissues as far as the vascular cambium, and grows predominantly intracellularly, especially within young secondary phloem. The formation of this close association with plant roots may represent a critical stage, concerned with elaboration of the ascocarps in the life cycle of this, otherwise 'putatively saprophytic fungus'. They mention that the localization of 'muffs' on parts of roots that are non-absorptive, suggests that the association is not truly mycorrhizal. However, the association that we have observed between species of morels and the herbaceous plants during the present studies, seem to be doubtlessly mycorrhizal as the fungus has been found to be associated with young absorbing roots.