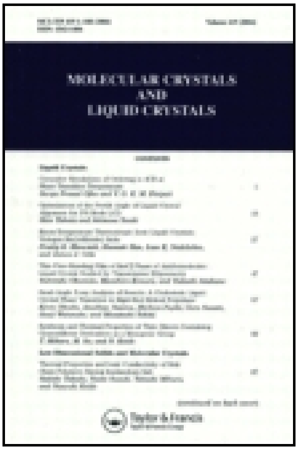

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Solvent Effects on Charge-Transfer Complexes in Solid Solutions

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Solvent Effects on Charge-Transfer Complexes in Solid Solutions

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Electrical and optical properties of a great variety of charge transfer complexes (CT) of organic compounds have been investigated in the recent years. The interest in this area is evidenced by large number of reviews and original reports. The studies of dark conductivity and photoconductivity have been recently extended to polymers acting as donors or acceptors, although more papers are related to the systems in which either the donor or acceptor consists of a low molecular weight species. Some studies have been carried out in which CT-complexes of polymeric species have been compared with the low molecular weight homologs. Little difference was found between these two types of complexes. The equilibrium constants of CT-complexes formation as determined from spectrophotometric studies, for polymeric species and for monomeric molecules were higher for the monomer than for the polymer (e.g. Refs 1–5). The charge transfer bands exhibited by the polymeric complexes did not always coincide with those of monomeric complexes. The increasing solvating power of the medium causes in general the red shift of the CT-band but in some cases the change of solvent polarity results in blue shift.[6,7] Thus various suggestions have been made in order to elucidate these effects. The solvent effect on several aromatic—TCNE CT-bands was carefully reexamined by Inokuchi *et al.*[8] and McRae's formula was used to interpret the observed CT-band shifts.

In the work described below studies of solvent effect were carried out with several solid solutions—polymers—in which different low molecular weight CT-complexes were dissolved. These systems present particular interest for studies of electrical properties and have potential practical applications. The spectroscopical properties of these solid solutions were compared with those of liquid solutions. The differences were discussed in function of temperature which in the case of solid polymeric matrices may be related not only to pure solvent effects but also to the glass transitions which in turn results in differences of mobility of polymer chain elements and may depend on anisotropy of the matrix induced by stretching.

EXPERIMENTAL

Low molecular weight components of CT-complexes: naphtalene, diphenyl, pyrene, durene, *t*-stilbene, carbazole and N-ethylcarbazole and tetracyanoethylene were purified by crystallization from suitable solvents, or sublimation. Polymers: PVC, PET, PPO, PS, PMMA, PBuA etc. were obtained from purified monomers by polymerization according to methods described in the literature, or when obtained from producers they were dissolved, precipitated and vacuum dried. The molecular weights were determined by viscometric method.

The refractive index (n) and dielectric constant (ε) values for the liquid solvents and the solid solvents—polymers—were taken from the literature data or determined. Spectrophotometric analyses were made with UV-Vis Spectrophotometer using silica cells with spacers and films of suitable thickness. The temperature dependence of the CT-band shifts were studies in thermostated cells or compartment with foils. In the case of liquid solutions the absorption spectra were recorded immediately ofter filling the cells. The anisotropy of polymeric films containing dissolved low molecular weight CT-complexes was obtained by stretching at suitable temperature. The photoconductivity studies of solid CT-complex solutions were carried out in vacuum using conventional equipment.

RESULTS AND DISCUSSION

The absorption spectra of the above mentioned CT-complexes in different polymeric matrices were first of all compared with those obtained in CCl_4 solution. In CCl_4 the shape and position of CT-maxima is in accordance with the data of Inokuchi *et al.*[8] Taking into consideration these data as well as those on the gaseous spectra given in the above mentioned paper the CT-bands in several liquid solutions of different dielectric constants and refractive indices are shifted to the red without changes of the shape. This suggests that the absorption maxima can be taken as the O—O band. The number of CT-maxima in liquid solution does not change as compared with the gas phase except for pyrene-TCNE and stilbene-TCNE solutions. The gas-to-solution shifts in nonpolar solvents do not exceed-5 kK and can be interpreted with the McRae relation for the solvent shift.[9] The plots made according to this relation enabled the constants in the McRae equation to be determined. The results show that the interaction between solute induced dipole or solute dipole and solvent induced dipole is rather large and a correlation between the n and ε values of the solvent and $\Delta h\nu_{CT}$ exists which was put in question by Offen and Abidi.[6] Using the constants obtained from McRae's formula applied to non-polar and polar solvents the solute dipole moments and solvent dipole moments interactions could be discussed.

In the case of solid solutions the general trend of $\Delta h\nu_{CT}$ is the same as in the case of liquid solutions if the solid solvents polymetric matrices are isorefractive with the liquid ones. This behaviour was found for polymeric matrices at temperature range exceeding their glass transition temperature Tg. Under these conditions the arrangement of solute molecules and polymer chain elements is similar to that of liquid solutions. The influence of the temperature changes on CT-band shift is similar to that which is found for liquid solutions because the mobility of the polymer chain elements enables the rearrangement of polymer segments. In the temperature range below the respective Tg values of a given polymeric matrix the temperature dependence of CT-band shift is different and is related to the free volume and mobility of side chains or small pendant groups. Some qualitative information on the solvent effects can be obtained when the solvatation effects on the absorption spectra shift are taken into consideration.[10–12] The rearrangement of solid solvent molecules depends in that case on the secondary glass transitions.

The use of C=O groups containing solvents was shown by Inokuchi *et al.*[8] to influence the $\Delta h\nu_{CI}$ in a different way, i.e. one observes blue shifts. This has been interpreted, by these authors, in terms of stereospecific solvatation. The same effect has been found in solid solutions of C=O group containing polymers. The effect of pressure on fluorescence and absorption spectra of aromatic compounds in the solid phase has been found.[13–15] These studies were devoted to crystals, mixed crystals and solid solutions in polymers. Similar conditions may be achieved in anisotropic films when the orientation of polymer chains in stretched films causes the decrease of distances between them (in the direction perpendicular to the stress applied) thus due to this effect one should expect the influence on the absorption spectra of dissolved CT-complexes. In reality a small shift of the CT-bands to the red was found which is however much smaller than that demonstrated by high pressure studies.

The photoconductivity studies of the above mentioned polymetric matrices with dissolved CT-complexes have shown that at constant illumination the change of nonpolar matrix does not manifest itself in the photosensitivity spectrum and in the intensity of photocurrents. The use of polar matrices in which the blue shift in CT-bands was found causes the change of the spectral photosensitivity and the intensity of the photocurrents. A special case which should be taken into consideration are the solid matrices where one of the components of the low molecular CT-complexes is capable of forming CT-complexes with the chain elements of the matrix for example stilbene—TCNE—polycarbonate system. The spectral and electrical properties change is thus not only related to the different kind of CT-complexes but also to the change of the mobility of macromolecular chain elements as it has been shown by the increase of β-glass transition temperature. Therefore it seems that the conclusions from studies of the solvent effects on CT-complexes in solid solution give valuable information leading to the understanding of the electrical properties of these systems.

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