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Molten-state Absorption Spectra of Weakly Interacting Donor-Acceptor Mixtures[1]

Jun-ichi AIHARA
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

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Synopsis. Absorption spectra of equimolecular mixutres of bulky electron donors, such as triphenylamine, and typical electron acceptors, such as *sym*-trinitrobenzene (TNB) and chloranil, in the molten state are reported. Though the components do not interact in the solid, the melts display distinct charge-transfer absorption bands in the visible region.

Several years ago, Hammond and Burkardt studied extensively various aspects of a series of weak donor-acceptor complexes.[2] According to their visual observations, some electron-donating molecules having bulky substituents do not form charge-transfer complexes with any of the typical electron acceptors in the solid state. A mixture of a bulky electron donor, such as triphenylamine, with most electron acceptors, however, has a deep color in the melt. The color of the melt vanishes on freezing, and the cycle can be repeated many times. In order to extend our understanding of this phenomenon, we measured the electronic spectra of this kind of donor-acceptor mixtures in the molten state.

Two bulky donor compounds, triphenylamine (TPA) and diphenylamine (DPA), were used in this study. The samples for the measurements of the solid- and molten-state spectra were prepared by solidfying the molten mixtures of the bulky electron donors with equimolar amounts of electron acceptors. The molten-state absorption spectra were taken near 150 °C at which temperature the mixtures were sure to be totally molten. The absorption spectra of the methylene chloride solutions were taken for comparison. A Beckman DK-2A spectrophotometer was used.

Figures 1–5 show the visible absorption spectra of mixtures of TPA with five electron acceptors. TPA is a pronounced example of a bulky electron donor. The gaseous ionization potential (I_g) of this compound is as low as 6.84 eV,[3] and it is customarily considered as an excellent electron donor. Furthermore, this compound is very suitable for the present experiment because it is thermally stable.

In general, the solution spectrum of the donor-acceptor mixture in the visible region displays an absorption band characteristic of a charge-transfer complex. Fortunately, absorption peaks of the charge-transfer bands were observed in the solution spectra of the two mixtures, the TPA-chloranil and the TPA-TNB. These absorption peaks ($h\nu_{CT}$) should be re-

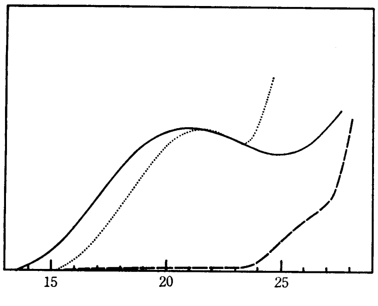

Fig. 1. The absorption spectra of the TPA-TNB mixture in the solid state (----), in the molten state (——), and in solution (······).

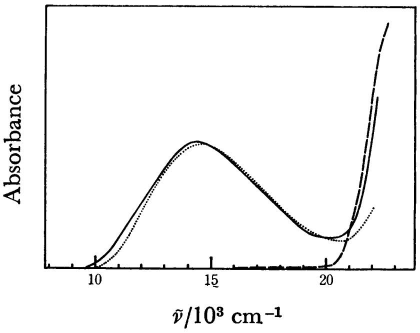

Fig. 2. The absorption spectra of the TPA-chloranil mixture in the solid state (----), in the molten state (——), and in solution (······).

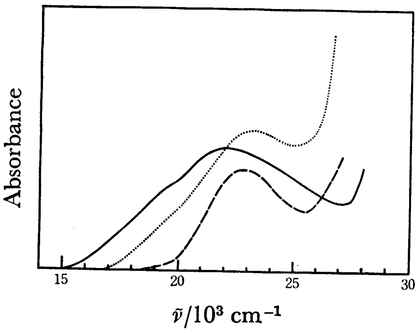

Fig. 3. The absorption spectra of the TPA-DMBQ mixture in the solid state (----), in the molten state (——), and in solution (······).

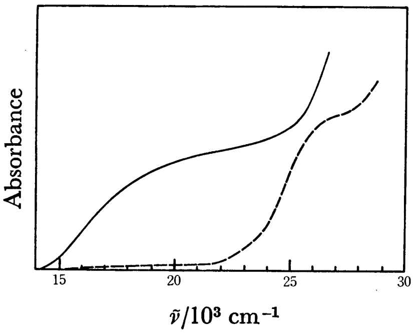

Fig. 4. The absorption spectra of the TPA-picric acid mixture in the solid state (----), and in the molten state (——).

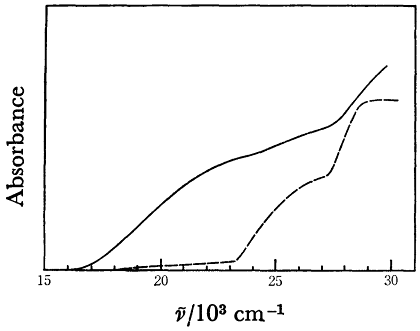

Fig. 5. The absorption spectra of the TPA-*m*-dinitrobenzene mixture in the solid state (----), and in the molten state (——).

produced by the empirical expressions such as:

$$h\nu_{\mathrm{CT}} = aI_g - b, \tag{1}$$

where a and b are constants associated with a given electron acceptor. For example, a and b are 0.853 and 3.51 eV, respectively, for a group of TNB complexes in chloroform. The absorption maximum of the TPA-TNB system in chloroform is located at 2.60 eV, whereas the value estimated from Eq. (1) is 2.32 eV. The deviation of the observed value from the estimated one is 0.28 eV. A deviation of this extent is properly ascribed to the bulky substituent effect, as was suggested before for the tetracyanoethylene complexes of methylbenzenes.[4]

On the other hand, the solid donor-acceptor mixtures appear almost colorless, indicating that the intermolecular charge-transfer interaction is substantially suppressed even in the domains of the solid solutions which may be present in the mixtures. The weak absorption tail which often appears in the energy region where there should be a charge-transfer band is supposedly due to incidental formation of a charge-transfer complex in the mixture.

An almost colorless mixture of TPA with TNB turned deep red on melting, and a mixture of TPA with chloranil was deep green in the molten state. Other molten mixtures were all reddish. This is in marked contrast to the behavior observed for ordinary charge-transfer complexes on raising the temperature above the melting point; in this case, the colored solid melts with little color change.[5]

As is shown in Figs. 1–5, the color change of the present mixtures is in accord with the appearance of the charge-transfer bands in the molten state. The absorption peaks are located at 20700 cm^{-1} for the molten TPA-TNB and at 14300 cm^{-1} for the molten TPA-chloranil. The astonishing coincidence of the spectral shapes between the molten-state and solution spectra strongly suggests that the colored species in the melt is similar to that in solution. In addition, the coincidence of the absorption peaks of the TPA-chloranil mixture in the melt and in solution suggests that the dielectric properties of the mixture, which are presumably associated with the solvatochromism of the charge-transfer band, are quite similar to those of the solvent (methylene chloride). Therefore, the intermolecular interactions appear to be still very weak in the melt. As was suggested by Lower for the solid complex,[6] the excitation might be localized in each donor-acceptor pair in the melt.

For the other molten mixtures containing TPA, the charge-transfer bands are found to overlap more or less with the absorption bands of the component molecules. For example, in the molten-state spectrum of the TPA-DMBQ (2,5-dimethyl-*p*-benzoquinone) system, the charge-transfer band is located above 15000 cm^{-1}, partially overlapping with the n-π^* transition of the benzoquinone. Since the relative intensities of both absorption bands are apparently comparable in the melt, the extinction coefficient of the charge-transfer band is estimated to be of the same order of magnitude as that of the n-π^* transition ($\varepsilon_{\max} = \sim 20$).[7] Such a small extinction coefficient is consistent with weak intermolecular interactions which are insufficient to form a complex in the solid state.

Mixtures of DPA with various electron acceptors display similar spectral changes on melting. However, they are very reactive in the molten state, and readily decompose. An absorption spectrum could be obtained of only the DPA-DMBQ mixture. Every aspect of the molten-state spectrum resembles that of the spectrum of the TPA-DMBQ mixture.

In a previous paper, we suggested that the charge-transfer interaction is not always a primary factor in determining the structure of the condensed phase.[8] It is noteworthy that the self-complex formation which is often attained to 100 percent in the *o*-anisyl-*p*-benzoquinone crystal is completely disturbed by the fluidity of the melt.[9] On the contrary, the fluidity of the melt is needed to allow the intermolecular charge-transfer interaction in the present donor-acceptor mixtures. Since the heat of complex formation (~0.30 kcal/mol)[2] is much less than the typical heat of sublimation (~30 kcal/mol),[10] the charge-transfer interaction, at all events, seems to be of secondary importance in the solid mixtures.

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