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T. Ito[a]; A. Kato[a]; S. Kobinata[a]
[a] Department of Materials Science, Toin University of Yokohama, 1614 Kurogane-cho, Aoba-Ku, Yokohama 225-8502, Japan,

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Charge transfer interaction between the nematogen 5CB and non-liquid crystal

T. ITO*, A. KATO and S. KOBINATA

Department of Materials Science, Toin University of Yokohama,
1614 Kurogane-cho, Aoba-Ku, Yokohama 225-8502, Japan

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In general, when a non-nematic solute is added to a nematic, the nematic–isotropic phase transition temperature (T_{NI}) decreases with increase in non-nematic concentration. But when there are hydrogen bonded complexes or π-complexes of suitable strength formed between the nematic and the solute molecules, the T_{NI} can rise. Mixing of *p*-terphenyl or anthracene with 5CB (4-cyano-4′-pentylbiphenyl) results in a T_{NI} rise. On the other hand, in a binary system consisting of a substance with strong acceptor properties (e.g. tetracyanoethylene; TCNE) and nematic 5CB, T_{NI} fell remarkably. We have now studied the effect of intermolecular interactions on the T_{NI} of 5CB by using various acceptor molecules and donor molecules as solutes. We have found that for binary systems in which 5CB and a solute molecule form distinct one-to-one complexes, T_{NI} falls rather rapidly. When the solute molecules have a strong acceptor power, the rate of T_{NI} fall with solute concentration is found to be correlated well with the electonegativity of the solute molecules.

1. Introduction

In general, when a non-nematic solute is added to a nematic, the nematic–isotropic phase transition temperature (T_{NI}) decreases with increase in non-nematic concentration [1–3], however it has been reported that, owing to hydrogen-bonded complexes formed between nematic 5CB and non-nematic solutes such as benzoic acid derivatives, T_{NI} rose [4, 5]; the increase in T_{NI} was ascribed to intermolecular hydrogen bonding interaction between the carboxyl group in the benzoic acid and the cyano group in 5CB. However, the stabilization energy of this hydrogen bonding is considerably smaller than that in a benzoic acid dimer, according to calculations using the semi-empirical molecular orbital method (MOPAC). In the benzoic acid/5CB binary system, benzoic acid is expected to exist almost totally as benzoic acid dimer, at least in concentrated solutions, and this was confirmed by IR measurements [6]. Recently, the importance of the ring dimer of an organic acid in the stabilization of a nematic state was reported by Kang and Samulski [7, 8]. In our study, because there is very little intermolecular hydrogen bonding interaction between 5CB and a benzoic acid dimer, the T_{NI} rise in such a binary system must be caused by intermolecular interactions other than hydrogen bonding between 5CB and the benzoic acid dimer. In order to ascertain this, we studied the phase behaviour of the 5CB and *p*-terphenyl binary system because *p*-terphenyl resembles the benzoic acid dimer in molecular shape and also has no hydrogen bonding power.

We reported in an earlier paper that T_{NI} rose in the *p*-terphenyl/5CB binary system [9], whereas the T_{NI} of tetracyanoethylene TCNE/5CB and biphenyl/5CB binary systems fell remarkably. These differences in T_{NI} changes were ascribed to the compositions of the charge-transfer (CT) complexes. In the case of *p*-terphenyl/5CB, the continuous variation method showed that there were cluster type complexes which result in a T_{NI} increase. In the case of TCNE/5CB and biphenyl/5CB, one-to-one complexes were mainly formed, which led to T_{NI} decreases [9, 10]. In this work, we have tried to make sure of the above points and also to investigate the relation between the T_{NI} changes and the strengths of the CT interactions. To this purpose, various solutes which act as electron donors or acceptors to 5CB were mixed with the nematogen 5CB.

We studied the thermal properties and compositions of the complexes in these binary systems. The rate of T_{NI} change in these binary systems was correlated with the electronegativities of the solute molecules, which were estimated on the basis of Mulliken's theory.

We found that a solute which acts as a π-electron acceptor to 5CB gives a clearly different correlation between the rate of T_{NI} change and the electronegativities from that of a donor. Furthermore we have found that

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*Author for correspondence; e-mail: fwhx2119@mb.infoweb.ne.jp

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in the binary system in which the CT band appears in the visible region and a one-to-one complex is formed, T_{NI} decreases remarkably.

2. Experimental

Commercial 5CB (Merck Japan) was used without further purification. Chloranil and the other substances (Tokyo, Kasei) were also used without further purification. The solutes used were 2,3-benztriphenylene, biphenyl, bromanil, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), tetrafluoroterephthalonitrile (TF-TPN) and chloranil.

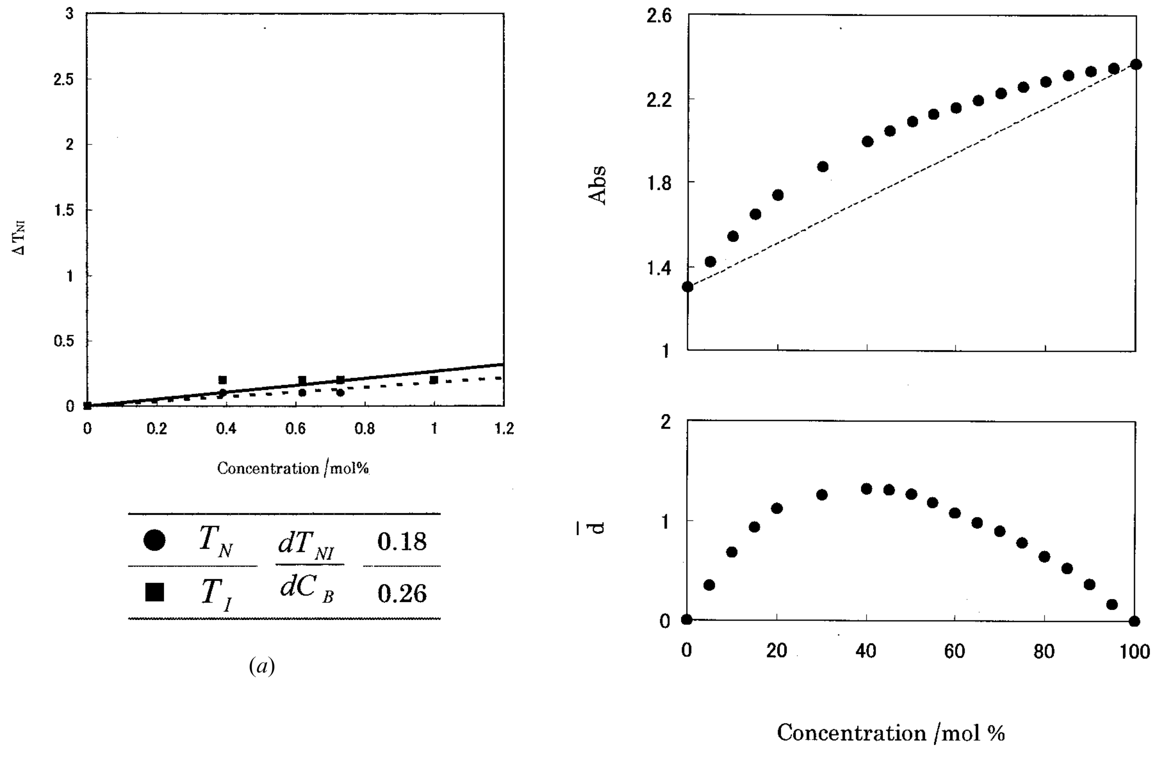
Absorption spectra were measured with a Shimadzu model UV-160A spectrophotometer, using cells having thicknesses of 5, 0.1, 0.02 and 0.01 cm. Nematic–isotropic transition temperatures of the dilute binary mixtures were measured by using a hot stage and polarizing optical microscopy.

3. Results and discussion

3.1. *The binary systems of 5CB with donor solutes*

Figures 1 and 2 show the results from thermal measurements (*a*) and the continuous variation method (*b*) in the binary systems consisting of various non-nematic donor solutes and the nematogen 5CB. Figures 1 (*a*) and 2 (*a*) show the results of the thermal measurements; the abscissa is the concentration of solute in mol % and the vertical axis plots the temperature difference between T_N and T_I of the binary systems and the clearing temperature of pure 5CB; T_N is the temperature at which the nematic phase begins to appear on heating; T_I is the temperature at which the nematic phase completely disappears on heating.

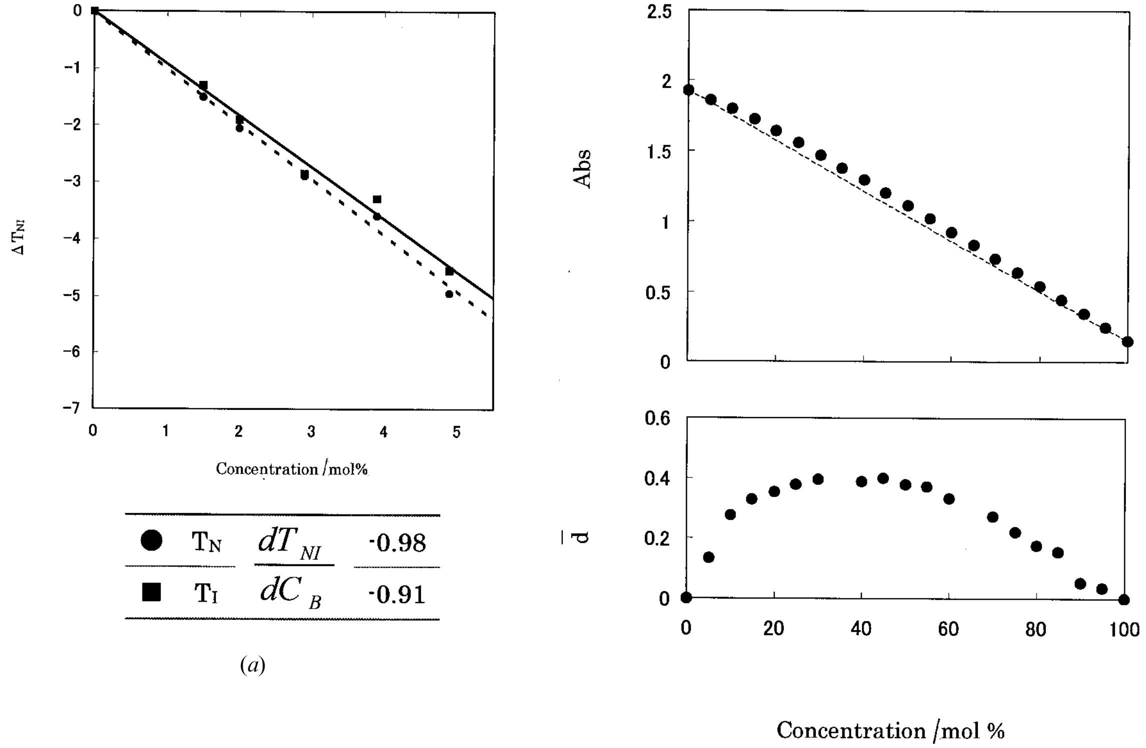
In figures 1 (*b*) and 2 (*b*) for the continuous variation method, the vertical axis of the upper figure is in each case the absorbance, and the figures below the horizontal axis represent the contribution of complex formation to the absorbance. Complex formation leads to the deviation from the straight dotted lines in the upper figures [9]. The composition of the π-complexes between biphenyl and 5CB was found to be two-to-three, see figure 2 (*b*), which is the same composition as those with 2,3-benztriphenylene/5CB and anthracene/5CB reported in the previous paper. In the latter two binary systems, T_{NI} slightly rose [9], but T_{NI} clearly decreases in the biphenyl/5CB system, see figure 2 (*a*). It is noted that the same two-to-three composition of the complexes gives a completely different behaviour; T_{NI} slightly rises in the



(*a*)

(*b*)

Figure 1. The results of thermal measurements (*a*) and the continuous variation method (*b*) for the 2,3-benztriphenylene/5CB binary system.



(*a*)

(*b*)

Figure 2. The results of thermal measurements (*a*) and the continuous variation method (*b*) for the biphenyl/5CB binary system.

2,3-benztriphenylene/5CB and anthracene/5CB systems, but decreases in the biphenyl/5CB system. This shows that T_{NI} change is not determined solely by the composition of the complexes.

The most probable intermolecular interaction explaining these effects is charge transfer interaction between 5CB and the solute because in some binary systems we could observe charge transfer bands in the visible region. One useful method of proving the importance of charge transfer interaction is to study the correlation of the rate of T_{NI} change with the electronegativity of the solute. If there exist definite correlations between the rate of T_{NI} change and the electronegativity of the solute molecules, the importance of CT-interaction will be proved. To estimate the electronegativities of all the solute molecules, including the solutes used in the previous paper, we carried out semi-empirical molecular orbital calculations by using MOPAC. The results are shown in the table.

The electronegativity of a molecule is calculated as the sum of the ionization energy (I_P) and the electron affinity (E_A) of the molecule. Part (*a*) of the table shows that 5CB solvent acts as an electron acceptor, and the solutes can act weakly as donors according to the $I_P + E_A$ data.

Table. Results from the continuous variation method, the rate of T_I change from thermal measurement, and the electronegativity of the molecules.

Solute	Composition	dT_I/dC	$(I_P + E_A)/\mathrm{eV}^a$
(a) Donor molecule to 5CB			
p-Terphenyl	complicated	0.55	9.51
Anthracene	2 : 3	0.07	9.43
2,3-Benztriphenylene	2 : 3	0.01	9.31
Biphenyl	2 : 3	− 0.85	9.28
Biphenylene	1 : 1	− 0.88	9.10
(b) Acceptor molecule to 5CB			
Bromanil	1 : 1	− 1.88	12.98
DDQ	1 : 1	− 1.71	13.00
TCNE	1 : 1	− 1.67	14.08
Chloranil	1 : 1	− 1.47	11.76
TF-TPN	1 : 3	− 1.88	13.39

[a] For solvent 5CB, $I_P + E_A = 10.13$ eV.

The sequence of the rate of T_{NI} change is well correlated with the electronegativity of the solute molecules. Figure 1 (*a*) shows that T_{NI} hardly depends on the concentration of solute in the anthracene/5CB [9] and 2,3-benztriphenylene/5CB systems.

3.2. *Binary systems composed of 5CB and acceptor solutes*

Figures 3, 4, 5 and 6 show the results of thermal measurements (*a*) and the continuous variation method (*b*) for binary systems consisting of various non-nematic acceptor solutes and the nematogen 5CB. Acceptor solutes studied in this work were TCNE, DDQ, bromanil, chloranil and TF-TPN used with 5CB as solvent. The CT-band appears in the visible range in these systems, except for the TF-TPN/5CB system. It may be hidden in the absorption band of the solute.

In figures 3, 4, 5 and 6, thick and thin lines show the absorption of the CT complexes and of the non-nematic solutes in the visible range, respectively. The compositions of these complexes and the T_{NI} changes in these systems were determined by the continuous variation method and by thermal measurements, as shown in figures 7, 8 and 9. The results for the TCNE/5CB system were reported in a previous paper [7].

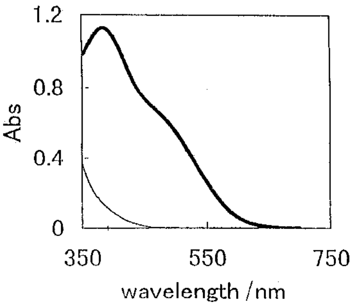


Figure 3. CT absorption band in the tetracyanoethylene (TCNE)/5CB system.

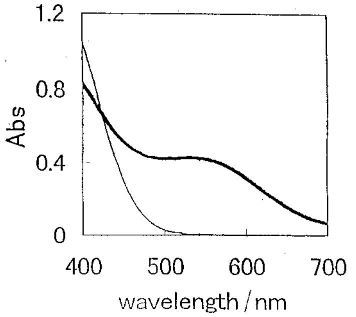


Figure 4. CT absorption band in the 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ)/5CB system.

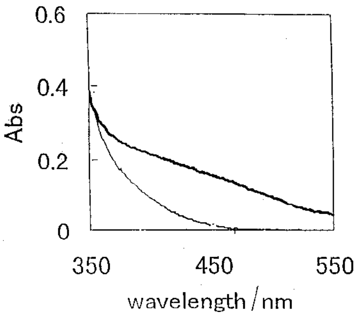


Figure 5. CT absorption band in the bromanil/5CB system.

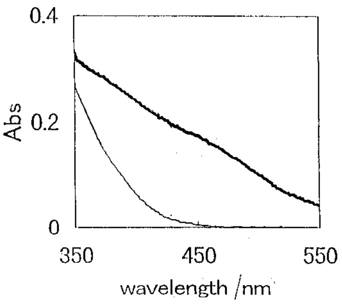


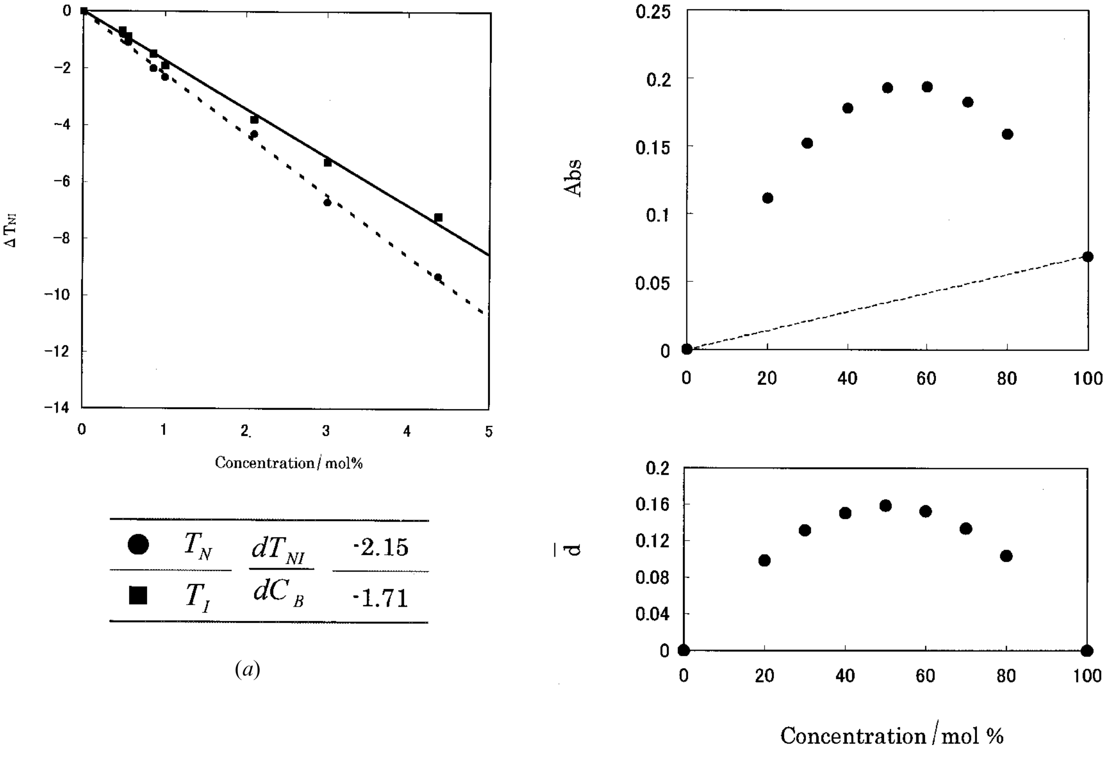
Figure 6. CT absorption band in the chloranil/5CB system.

The composition of π-complexes in the TCNE/5CB, DDQ/5CB, bromanil/5CB and chloranil/5CB binary systems were found to be 1 : 1. On the other hand, the composition of the TF-TPN complex was found to be 1 : 3. T_{NI} in all these systems decreases remarkably faster than in the binary systems in which electron donor solutes were mixed with 5CB. The compositions of the complexes, the rates of T_{NI} change and the electronegativities of the acceptor molecules calculated by MOPAC are summarized in part (*b*) of the table. The rate of T_{NI} change is well correlated with the electronegativity of the solute molecules in a similar way to that in the table (*a*). Comparison of the results on the electron donor and acceptor solutes shows that the T_{NI} changes depend on the strength of the π-intermolecular interaction, as well as the composition of the π-complex.

3.3. *Correlation between the rate of T_I change and the electronegativity of the molecules (χ_M)*

All the results for the rate of T_I change by π-intermolecular CT interactions are plotted in figure 11 against the electronegativities of the molecules (χ_M). In figure 11, the abscissa is the rate of T_I change, the vertical axis plots χ_M of the solutes and the dotted horizontal line represents χ_M of the 5CB molecule.

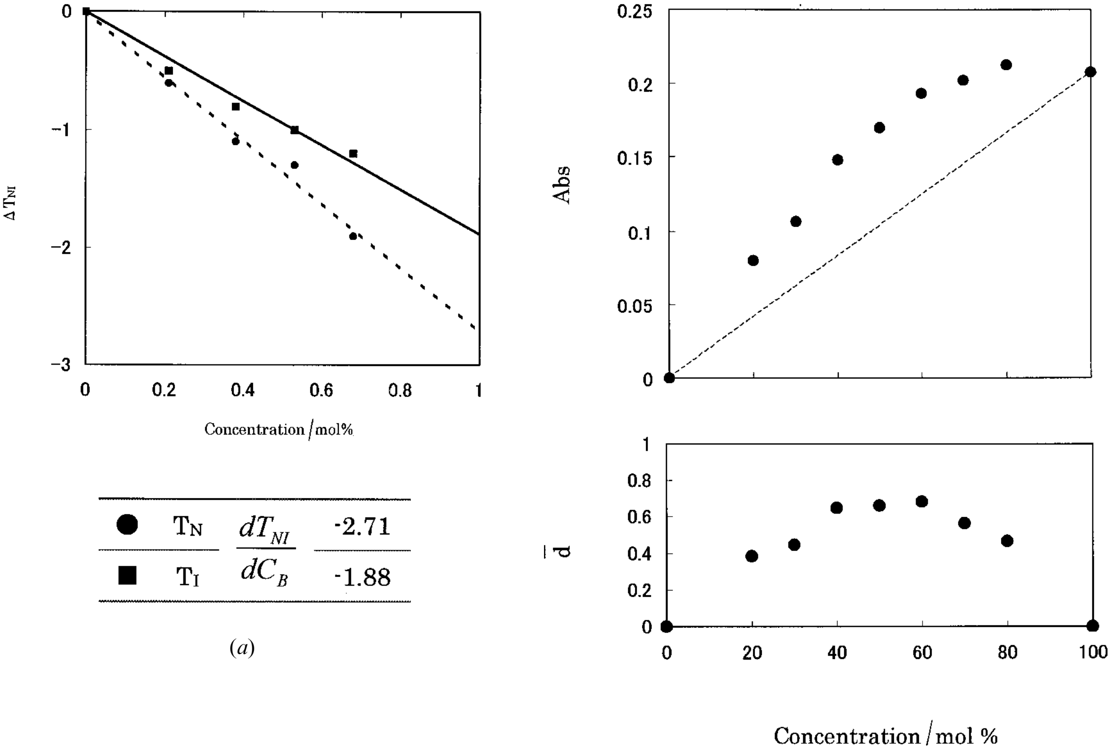
This figure shows four points in the right hand T_{NI}-rising region. These four solutes are anthracene, *p*-terphenyl, 4-nitro-*p*-terphenyl and 2,3-benztriphenylene. It is noted that these solutes have more than three rings in the molecules and have χ_M values close to that of 5CB. Furthermore the composition of the complexes for these solutes with 5CB is not 1 : 1. In the left hand, T_{NI}-falling region in figure 11 there are two distinct regions. The solutes in the upper region act as electron acceptors to 5CB. In this region, the stronger the acceptor power of the solutes, the faster T_{NI} falls. This means that the stronger the CT-complex, the faster T_{NI}



(*a*)

(*b*)

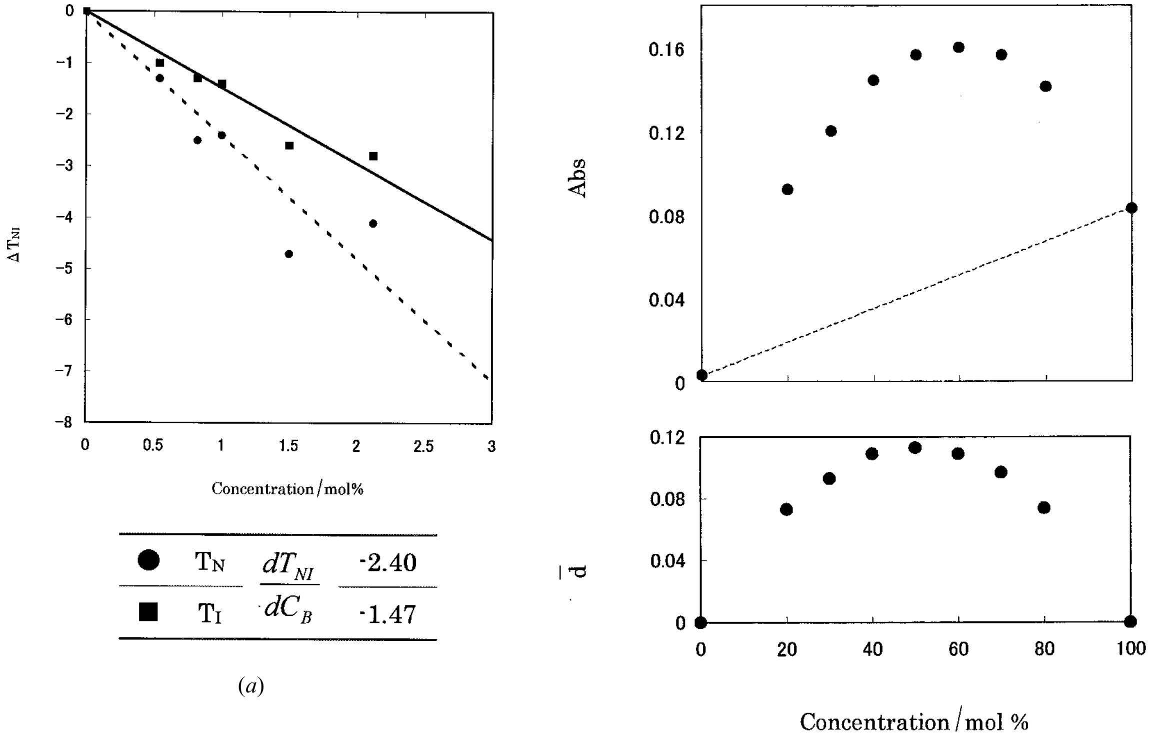
Figure 7. The results of thermal measurements (*a*) and the continuous variation method (*b*) for the DDQ/5CB binary system.



(*a*)

(*b*)

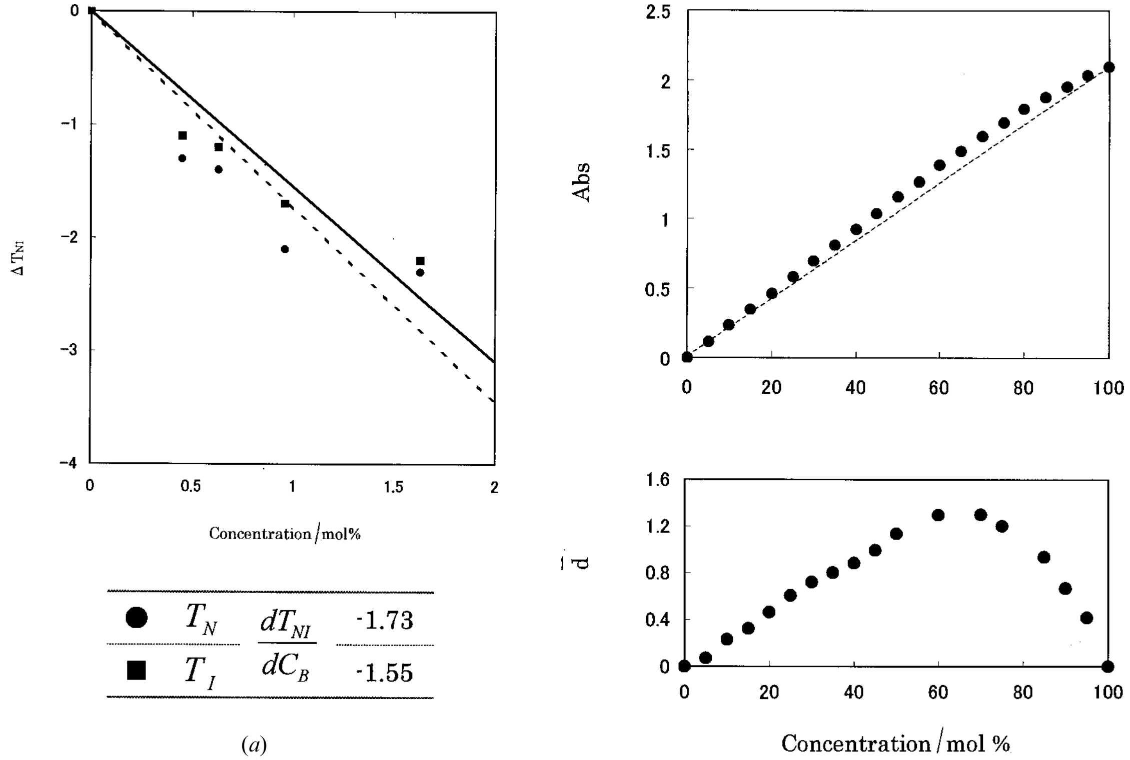
Figure 8. The results of thermal measurements (*a*) and the continuous variation method (*b*) for the bromanil/5CB binary system.



(*a*)

(*b*)

Figure 9. The results of thermal measurements (*a*) and the continuous variation method (*b*) for the chloranil/5CB binary system.



(*a*)

(*b*)

Figure 10. The results of thermal measurements (*a*) and the continuous variation method (*b*) for the TF-TPN/5CB binary system.

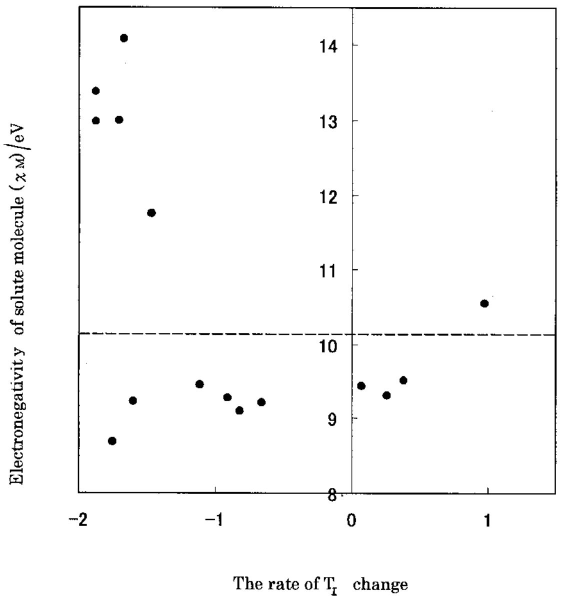


Figure 11. The correlation between T_I change and electronegativity for the solute molecule.

decreases. It is noted that the solutes in this region include the solute which makes a 1:3 complex with 5CB (TF-TPN).

The solutes in the lower region act as electron donors to 5CB, and the figure shows that although negativity change for molecules is not too large, the rate of T_{NI} change is rather widely distributed.

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