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Electrical Properties and Constitution of Several Low-resistivity Iodine Complexes

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The electrical resistivity and Seebeck coefficient of the iodine complexes with eight aromatic compounds were examined as functions of the composition and the temperature. The formation of complexes is indicated by maxima or shoulders in the resistivity-composition isotherms at the following compositions: (anthanthrene)$_2$I$_9$, (6,12-dioxoanthanthrene)I$_2$, (6,12-dioxoanthanthrene)I$_3$, (pyranthrene)I$_3$, (violanthrene)$_2$I$_7$, (phthalocyanine)I$_2$, (phthalocyanine)I$_5$, (phenoxazine)$_2$I$_3$, (pyridazine)$_5$I$_9$, and (*N*,*N*′-diphenyl-*p*-phenylenediamine)$_5$I$_{13}$. Furthermore, some sharp resistivity minima are considered as evidence of the complex formation: *e.g.*, (6,12)-dioxoanthanthrene)$_2$I$_3$ and (phthalocyanine)$_2$I$_3$. On the basis of these compositions, a nonintegral formal oxidation state for the organic molecules and the presence of iodine as triiodide or higher polyiodide ions are established for most of the complexes.

In an earlier report from this laboratory, it was demonstrated that the careful examination of the electrical properties as functions of the composition is a powerful tool for elucidating the constitution of semiconducting thiazine–iodine complexes.1) For example, the resistivity-composition isotherm of the phenothiazine–iodine system shows a shoulder as high as 800 Ω cm at a composition of two molecules of the thiazine to five atoms of iodine and also a minimum as low as 20 Ω cm at a composition of one molecule to three atoms. Moreover, a decrease in the activation energy for semiconduction by a factor of a half and a change in the sign of the Seebeck coefficient from negative to positive can be observed at the former composition. The similarity in vibrational spectrum between the iodine complex and the complex cation radical bromide of the 2 : 1 type, together with the above-mentioned electrical features, led us to propose the formation of a complex cation radical pentaiodide, $(C_{12}H_9NS)_2{}^+I_5{}^-$. The complex deposited from solutions is of a mole ratio of 2:3 and deviates as much as a half mole of iodine from this composition. There is no doubt that this amount of extra iodine plays an important role in the occurrence of the unusually low electrical resistivity. In the present paper, we wish to summarize the results of analogous studies on the iodine complexes with the following eight aromatic compounds: anthanthrene (dibenzo[*def*, *mno*]chrysene), 6,12-dioxoanthanthrene, pyranthrene, violanthrene, 29*H*,31*H*-phthalocyanine, phenoxazine, pyridazine, and *N*,*N*′-diphenyl-*p*-phenylenediamine (see the structural formulas given in Fig. 1). The composition ranges examined here were limited mostly by the thermodynamic instability of the iodine-rich complexes. Nevertheless, we believe that our study could cover the low-resistivity complexes in which we were interested.

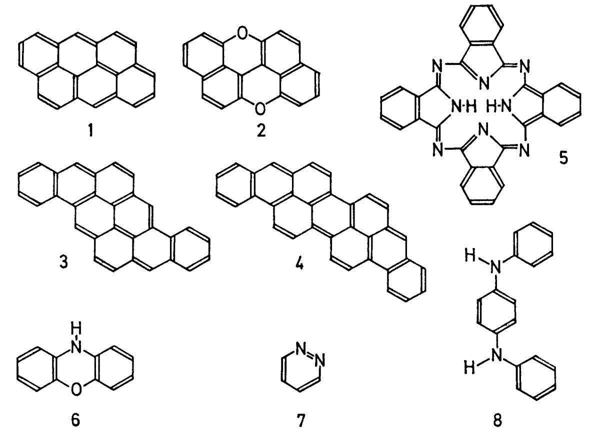


Fig. 1. Structural formulas of the organic component compounds; 1) anthanthrene, 2) 6,12-dixoanthanthrene, 3) pyranthrene, 4) violanthrene, 5) 29*H*,31*H*-phthalocyanine, 6) phenoxazine, 7) pyridazine, and 8) *N*,*N*′-diphenyl-*p*-phenylenediamine.

Before presenting the results, we wish to review briefly the electrical behavior of mixtures. If two coexisting phases are strictly stoichiometric and mechanically mixed without interaction, the logarithmic mixing rule may apply for the resistivity. The composition of a distinct complex may correspond to a minimum in the resistivity-composition isotherm if its resistivity is lower than those of the neighboring complexes, or a maximum if its resistivity is higher. On the other hand, the behavior may depend quite differently upon the composition, when the incorporation of a marked stoichiometric imbalance is conceivable for a given phase. As additional carriers are introduced by the imbalance, the stoichiometric composition of a low-resistivity complex may be indicated by a sharp maximum rather than a minimum in the isotherm. In such a case, the nearby minima may be considered to be indicative of the lower and upper limits of the deviation from stoichiometry. When the maximum is too low to be detected, the appearance of a rather broad minimum covering the stoichiometric composition may be expected. Therefore, the formation of complexes can be undoubtedly established by maxima appearing in the resistivity-composition isotherm but not necessarily by minima.

Experimental

Materials. The anthanthrene obtained commercially was reduced to the hydrocarbon by the zinc-dust fusion method.2) Anthanthrene thus prepared was purified by repeated sublimation in a vacuum. 6,12-Dioxoanthanthrene was synthesized starting from 2,2′-binaphthol, as described by Pummerer *et al.*[3] Pyranthrene was obtained by the reduction of commercial pyranthrone with zinc dust, pyridine, and acetic acid.[4] By vacuum sublimation through a thin layer of activated alumina the hydrocarbon became orange colored. The violanthrene, supplied some twenty years ago by Prof. Junji Aoki, now of Toho University, was purified by sublimation in a vacuum. Phthalocyanine, pyridazine, and *N*,*N*′-diphenyl-*p*-phenylenediamine employed in the present work were commercial products. The diamine was recrystallized from ethanol. Phenoxazine was prepared by the condensation of *o*-aminophenol in the presence of iodine.[5] All the iodine complexes, unless otherwise stated, were obtained by careful grinding of the weighed organic compound or complex of a known composition and iodine in an agate mortar in the presence of a small amount of benzene. The phthalocyanine complexes were made by boiling a benzene solution of iodine with powdered phthalocyanine. The iodine contents were determined by microanalysis.

Measurements. The electrical resistivities and Seebeck coefficients of polycrystalline compactions were recorded as functions of the temperature.[1]

Results and Discussion

Anthanthrene–Iodine. As early as 1939, Brass and Clar reported the isolation of the triiodide from a benzene solution;[6] however, no attention has been paid to the electrical properties. In Fig. 2, the electrical resistivity values at 20 °C are plotted against the number of iodine atoms per anthanthrene molecule, *n*. The shaded circles indicate that the samples were treated with a boiling benzene solution of iodine. They might therefore be more homogeneous than those indicated by open circles. There are a maximum of about 20 Ω cm at $n=4.5$ and minima of about 7 Ω cm near $n=4$ and 5 in the resistivity-composition isotherm. This behavior appears to be indicative of the nonstoichiometric nature of the complex. The formation of (anthanthrene)$_2{}^+$I$_9{}^-$ may be deduced from the location of the maximum. The incorporation of an excess of either the hydrocarbon or iodine of as much as a half mole into this complex appreciably decreases the resistivity. It must be added that no anomalous features were noted at the composition reported by Brass and Clar, namely $n=3$. The temperature dependence of the resistivity, ρ, follows the typical semiconductor behavior: $\rho=\rho_0\exp(E/kT)$. The values of the activation energy for semiconduction, E, near room temperature are mostly in the range from 0.05 and 0.07 eV. No abrupt change could be detected even at the composition of the resistivity maximum.

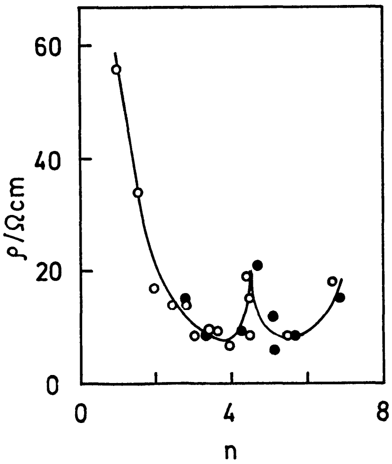


Fig. 2. Electrical resistivity at 20 °C plotted against the iodine content in the anthanthrene-iodine system. The shaded circles indicate that these samples were treated with a boiling benzene solution of iodine.

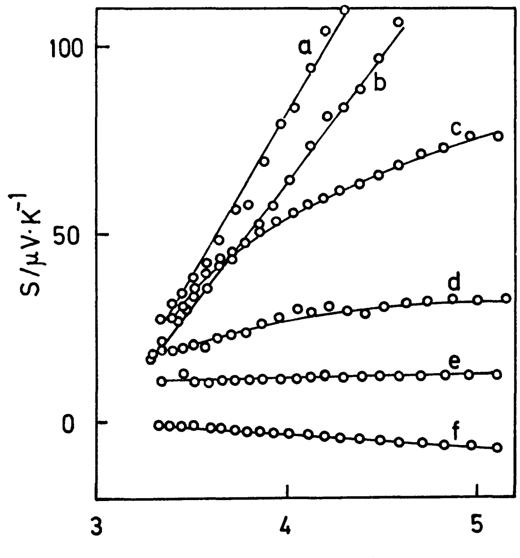


Fig. 3. Seebeck coefficient of the anthanthrene-iodine complexes; a) $n=1.51$, b) 3.70, c) 4.23, d) 4.41, e) 5.07, and f) 6.68.

The variation of the Seebeck coefficient, *S*, with the reciprocal temperature for six representative samples is illustrated in Fig. 3. Among them, samples b, c, and e are those indicated by shaded circles in Fig. 2. The variation depends markedly upon the composition. At $n=1.5$, a linear relationship with the reciprocal temperature is observed over the whole range (see Curve a). The positive slope may indicate that the contribution of holes to the conduction is larger than that of electrons. By the incorporation of additional iodine the slope in the low-temperature range becomes more gentle. As is shown by Curves c and d, such a tendency is especially large when the composition is close to the above-mentioned complex. The coefficient becomes essentially independent of the temperature near $n=5$ and then changes not only its sign but also the sign of the slope (see Curves e and f). These observations may imply that the ratio of the electron mobility to the hole mobility is nearly unity in the phase of (anthanthrene)$_2$I$_9$. The Seebeck coefficient at −23 °C is plotted against *n* in Fig. 4. The values are rather scattered; nevertheless, it is evident that the coefficient decreases almost linearly with *n* and becomes zero near $n=6$. As is readily understood from Fig. 3, this slope and the composition where the coefficient changes its sign is not independent of the temperature.

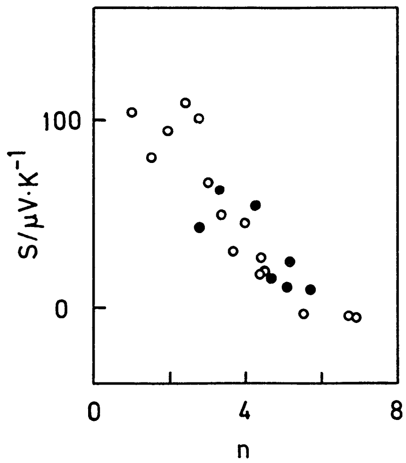
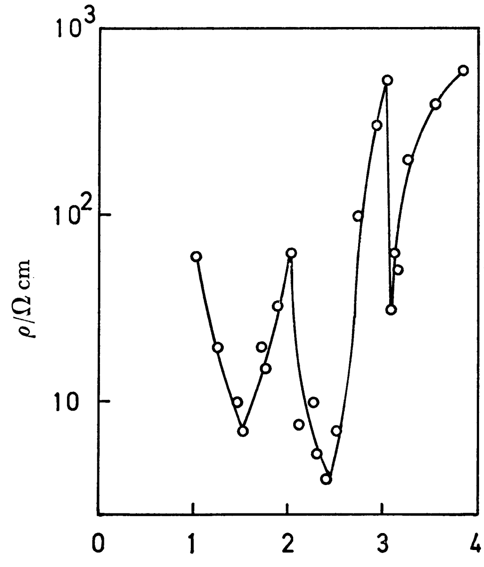


Fig. 4. Seebeck coefficient at −23 °C plotted against the iodine content in the anthanthrene-iodine system. As to the shaded circles, see the caption of Fig. 2.

6,12-Dioxoanthanthrene–Iodine. This compound has the same framework as anthanthrene and has been reported to form a monoiodide by Brass and Clar.[6] The introduction of two oxygen atoms into the framework gives rise to significant localization of the electrons in the highest occupied level, as revealed by a decrease in the total span of the ESR spectrum.[7] In view of these facts, it seemed to be of interest to compare the formation of iodine complexes of these two component compounds.

As is shown in Fig. 5, the resistivity is far more sensitive to the composition than that in the anthanthrene–iodine system. Note that the scale on the ordinate is logarithmic. One maximum with a resistivity of about 60 Ω cm, is located at $n=2$ and the other one at $n=3$. The latter is about tenfold higher than the former. As the ionization potential is known to be close to that of anthanthrene,[7] the formation of cation radical salts is more likely than the formation of molecular adducts. Therefore, the products corresponding to these n values may be (6,12-dioxoanthanthrene)$_3{}^{2+}$(I$_3{}^-$)$_2$ and (6,12-dioxoanthanthrene)$^+$I$_3{}^-$. Thus, the compound differs considerably from anthanthrene in the behavior of iodine complex formation. It is not clear to what extent the former compound is nonstoichiometric. The sharp minima located at $n=1.5$ and 2.5 might be an indication of the formation of (6,12-dioxoanthanthrene)$_2{}^+$I$_3{}^-$ and (6,12-dioxoanthanthrene)$_2{}^+$I$_5{}^-$. The minimum appearing a little above $n=3$ may be due to the nonstoichiometry of the phase at $n=3$. The effect of an excess of the component on the resistivity is so pronounced that the ratio of the value at $n=3$ to that at the last minimum is more than ten. The activation energy for semiconduction in the range from $n=1$ to 3 is 0.08—0.12 eV. At higher iodine contents, a gradual increase is found, reaching almost 0.2 eV by $n=4$.



Fih. 5. Electrical resistivity at 20 °C plotted against the iodine content in the 6,12-dioxoanthanthrene–iodine system.

The Seebeck coefficient of this system is independent of the temperature up to $n=2$. The coefficient is as much as +220 μV K^{-1} at $n=1$ and is reduced by a factor of a half by $n=1.5$ and further by the same factor by $n=2$. Above this composition, a positive slope is noted in the plot of S against the reciprocal temperature. The slope becomes steeper as n increases; therefore, the room temperature value changes its sign near $n=3.5$ and is −40 μV K^{-1} at $n=4.9$, which is the highest iodine content examined. In this system, holes appear to be the major carriers in the whole composition range.

Pyranthrene–Iodine. This hydrocarbon is known to form black complexes with bromine and iodine.[8,9] The ESR absorption and the electrical resistivity of the iodine complex were reported for a composition of $n=4$.[9,10] The resistivity-composition isotherm at room temperature is presented in Fig. 6. The presence of a maximum of 35 Ω cm at $n=3$ and minima at $n=$ 2.5 and 3.5 is clearly noted; therefore, the formation of a simple cation radical triiodide, (pyranthrene)-I$_3$, is feasible. We failed to obtain samples with $n>4$. The activation energy for semiconduction is about 0.06 eV throughout the examined composition range.

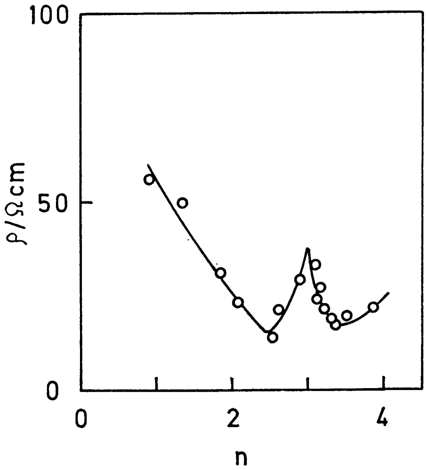


Fig. 6. Electrical resistivity at 20 °C plotted against the iodine content in the pyranthrene-iodine system.

The Seebeck coefficients at room temperature are scattered in a narrow range of $+5$ to $+10$ μV K^{-1} and decrease linearly with the reciprocal temperature at all the compositions. Although the slope tends to be steeper and negative values are observed at low temperatures when n is small, the dependence on the composition is not large enough to find out the correlation between S and n at any temperature.

Violanthrene–Iodine. The formation of the bromine and iodine complexes was described in 1955.[11] The latter is very stable and is one of the halogen complexes most extensively studied in those days. The diamagnetic susceptibility of the violanthrene–iodine system was shown to vary linearly with the halogen content, but the value was found to be markedly less than the one estimated by the application of the additivity rule. The deviation reaches its maximum at $n=4$.[11] The ESR study made later revealed the presence of just enough unpaired electrons to account for the observed deviation.[9] The resistivity-composition isotherm published in 1956 has a broad minimum around $n=4$, the value at this composition being 40 Ω cm.[8] The complex was concluded to be nonstoichiometric on the basis of the equilibrium concentration of iodine in carbon tetrachloride, examined as a function of the composition of the solid complex.[12] No sharp peak was observed in the X-ray diffraction pattern of the samples with $n \simeq 4$, suggesting that they are amorphous.[12]

Figure 7 presents the newly-determined resistivity-composition isotherm at room temperature. The shaded circles indicate that these samples were prepared by the treatment of the powdered hydrocarbon with a boiling benzene solution of iodine. This is the method in the previous work for the preparation of a complex.[8,11,12] Contrary to the diagram reported earlier, a maximum can be located at $n=3.5$ and minima around $n=3$ and 4. The observed feature is consistent with the reported nonstoichiometry; the idealized composition may be expressed by the formula $(\text{violanthrene})_2{}^+\text{I}_7{}^-$. The upper limit of the homogeneity range of this complex is probably near $n=4$. The activation energies for semiconduction were scattered in a range from 0.08 to 0.12 eV and the correlation with the composition could not be established.

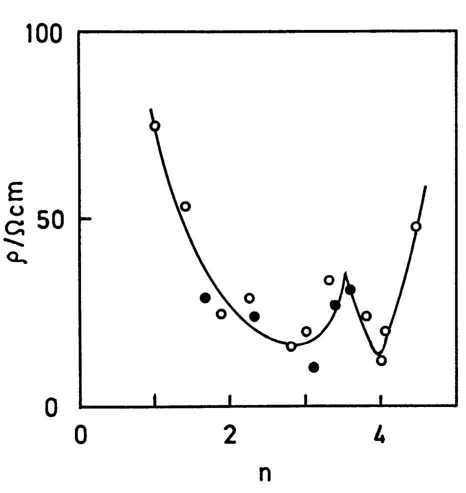


Fig. 7. Electrical resistivity at 20 °C plotted against the iodine content in the violanthrene-iodine system. The shaded circles indicate that these samples were prepared in a boiling benzene solution of iodine.

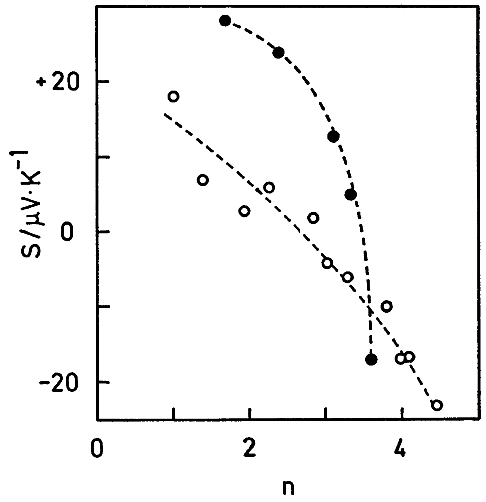


Fig. 8. Seebeck coefficient at 20 °C plotted against the iodine content in the violanthrene-iodine system. As to the shaded circles, see the caption of Fig. 7.

As is shown in Fig. 8, the room-temperature value of the Seebeck coefficient is positive at $n=1$ and decreases as the iodine content increases. In contrast to the electrical resistivity, the Seebeck coefficient of this system is significantly affected by the method of sample preparation. The open circles and shaded circles are clearly on different curves. The change of the sign occurs below $n=3$ for the samples indicated by open circles, while almost at $n=3.5$ for the samples indicated by shaded circles. When the coefficient is plotted against the reciprocal temperature, the slope in the high-temperature region is negative throughout the examined composition range and becomes more gentle as the iodine content increases. The value tends to saturate at low temperatures. This tendency is observed at higher temperatures when the complex contains more iodine.

Contrary to an earlier observation that the specific volume of the complex with $n<4$ is larger than the sum of the specific volumes of the constituents,[12] no deviation from the additivity could be detected with our polycrystalline compactions.

29H,31H-Phthalocyanine–Iodine. The resistivity of phthalocyanine has been shown by Aoyagi *et al.* to be considerably lowered by the addition of a small amount of iodine.[13] The dark solids obtained by the oxidation of a number of metal phthalocyanines by iodine have been reported to exhibit resistivities of the order of 0.1 to 1 Ω cm by Petersen *et al.*[14] The exact composition of their iodine complexes has been noted to depend on the preparation conditions.

The resistivity-composition isotherm of the phthalocyanine–iodine system presented in Fig. 9 shows a maximum at $n=2$, a shoulder at $n=5$, and minima, at $n=1.5$ and about 6. On the basis of these findings the presence of phases expressed by $(\text{phthalocyanine})_3{}^{2+}(\text{I}_3{}^-)_2$ and $(\text{phthalocyanine})^+\text{I}_5{}^-$ seems to be certain. The activation energy for semiconduction

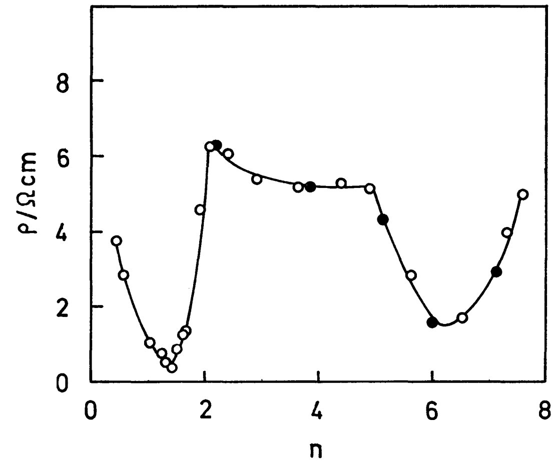


Fig. 9. Electrical resistivity at −23 °C plotted against the iodine content in the phthalocyanine–iodine system. The shaded circles indicate that these samples were made by the addition of iodine to those shown by open circles.

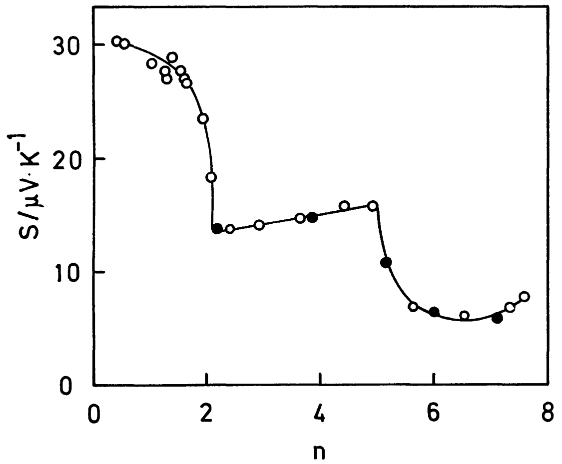


Fig. 10. Seebeck coefficient at −23 °C plotted against the iodine content in the phthalocyanine–iodine system. As to the shaded circles, see the caption of Fig. 9.

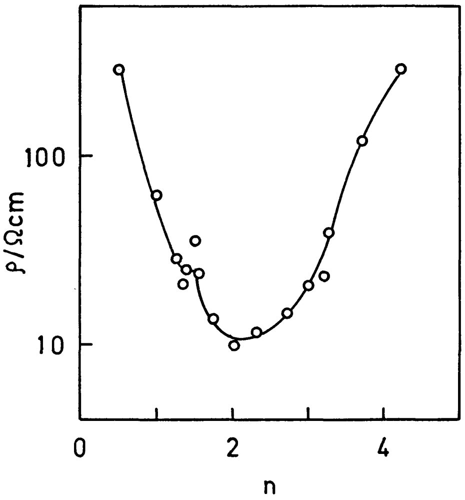


Fig. 11. Electrical resistivity at 20 °C plotted against the iodine content in the phenoxazine–iodine system.

is as small as 0.015 eV up to $n=1.5$ and then sharply increases to 0.05 eV by $n=2$. Therefore, the compound, $(\text{phthalocyanine})_2^+\text{I}_3^-$, may be formed in this system. Between $n=2$ and 5 the activation energy stays around 0.04 eV and then around 0.03 eV.

The Seebeck coefficient is positive for all the samples prepared and over the temperature range examined. The slope is mostly negative when plotted against the reciprocal temperature. As is shown in Fig. 10, the values at −23 °C ($10^3/T=5$) are between $+27$ and $+30$ μV K^{-1} up to $n=1.5$ and then sharply decrease by a factor of a half by $n=2$. Between $n=2$ and 5 the values remain around $+15$ μV K^{-1}. Above $n=5$, the coefficient decreases again by a factor of a half. In the last iodine-content range, the Seebeck coefficient shows an increase at low temperatures.

Phenoxazine–Iodine. The organic constituent is structurally related to phenothiazine studied in our previous work[1] and is known to form an iodine complex, the composition of which is the same as that of the sulfur analog; that is, $n=3$.[15] Nevertheless, the resistivity-composition isotherm presented in Fig. 11 is distinctly different from that of the phenothiazine–iodine system. A shoulder is located at $n=1.5$ instead of $n=2.5$. Furthermore, the minimum is found at $n=2$ instead of $n=3$. No anomalous feature is observed at $n=3$, which is the composition of the complex crystallized from a benzene solution. The overall appearance is less dramatic; that is, the resistivity at the shoulder is only about threefold larger than that at the minimum. On the other hand, the corresponding ratio in the sulfur analog–iodine system is as much as forty. The activation energy for semiconduction is about 0.13 eV throughout the examined composition range.

The Seebeck coefficient at 20 °C was reported to be slightly positive at $n=3$ and to decrease drastically by lowering the temperature. The coefficient in the composition range of $n=1$—1.5 is about -10 μV K^{-1} and independent of the temperature. When n is increased to 1.5, the room-temperature value is unchanged but the slope is slightly negative against the reciprocal temperature. Above $n=1.5$, the slope becomes increasingly negative. As the dependence on the composition near room temperature is rather small, the coefficient at 70 °C is plotted against n in Fig. 12. The sign changes from negative to positive near $n=1.5$.

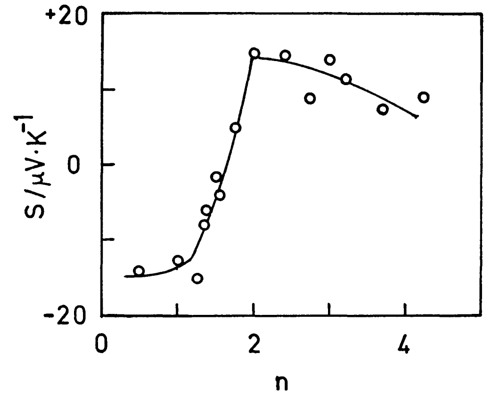


Fig. 12. Seebeck coefficient at 70 °C plotted against the iodine content in the phenoxazine–iodine system.

Of course, the behavior depends markedly upon the temperature selected. If one chooses a low temperature, say −70 °C, the sign is negative over the whole range of n; however, an abrupt change of magnitude may be found above $n=1.5$. The results described above clearly indicate the formation of a complex at $n=1.5$, while no support for the existence of a complex at $n=3$ could be obtained by the present method.

Although the vibrational spectrum could not be examined with the complex crystallized from a benzene solution because of the difficulty of pulverization,[15] samples prepared for this work are composed of fine powders and allow such measurements. As is known for this kind of materials, the spectrum in the rock-salt region is dominated by the electronic absorption. At $n=1.75$, the observed vibrational bands are broad and give a pattern very different from that of the parent organic compound. When a large amount of iodine is added to this sample, say $n>5$, a pattern consisting of sharp bands is recorded. By analogy with the case of the phenothiazine–iodine, the latter spectrum may be assigned to the monopositive ion of phenoxazine. The complex formed at $n=1.5$ is perhaps a complex cation radical salt which can be expressed by $(\text{phenoxazine})_2{}^{+}I_3{}^{-}$.

Pyridazine–Iodine. Hoare and Pratt have reported that a pyridazine molecule combines with 2—2.8 atoms of iodine to form a black solid and that the resistivities measured using two-probe technique fall in the range of 1—50 Ω cm at room temperature.[16] This organic compound has the lowest molecular weight among the compounds known to form low-resistivity iodine complexes.

There are a peak at $n=1.8$ and minima at about $n=1.6$ and 2 in the resistivity-composition isotherm shown in Fig. 13. The activation energy for semiconduction shows also a discontinuous change at $n=1.8$; namely, the value up to this composition is about 0.035 eV and then suddenly drops to about 0.02 eV. These observations unambiguously establish the idealized composition of a complex in this system, $(\text{pyridazine})_5I_9$. Though the present work provides no evidence for the nature of the iodine, it is likely that the iodine is in the form of a triiodide ion. If so, the above-mentioned product may be expressed by $(\text{pyridazine})_5{}^{3+}(I_3{}^{-})_3$. The resistivity observed near $n=2$, which may be the upper limit of the homogeneity range including the maximum or may be in an entirely different phase, is as low as 0.4 Ω cm. The Seebeck coefficient is essentially unchanged by the temperature and is scattered in a narrow range of +3 to +10 μV K^{-1}.

N,N′-*Diphenyl*-p-*phenylenediamine–Iodine.* This is one of the iodine complexes of oligoanilinic derivatives extensively studied by Honzl *et al.*[17] The crystal structure of this complex with $n=2.4$ has been analysed by Huml.[18] The diamine molecules are arranged one below the other in layers spaced 3.77 Å apart and the iodine atoms are arranged in chains almost perpendicular to the layers. On the basis of the distribution of distances of iodine atoms, the chains are considered to consist of triiodide ions. Hádek *et al.* have reported the electrical and magnetic properties of the complex with the above-mentioned composition.[19—21] According to their work, the activation energy for semiconduction observed with polycrystalline compactions is 0.07 eV in the temperature range of −50 to +50 °C and 0.21 eV below this range. The Seebeck coefficient is negative near room temperature and changes sign below −70 °C. In addition, the measurements on a complex with $n=2$ are available due to the of work of Sano *et al.*[22] They have concluded that the conductivity due to electrons is larger, but only slightly, than that due to holes; however, the work described below indicates that the behavior may not be so simple as they supposed.

As is illustrated in Fig. 14, the room-temperature resistivity gradually decreases by the increase of iodine content up to $n=2$ and then increases by a factor of ten between $n=2.4$ and 2.6. The value in the range of $n=1.8$ to 2.4 is 4—5 Ω cm. There is a shoulder at $n=2.6$. The activation energy for semiconduction near room temperature is about 0.07 eV over the range

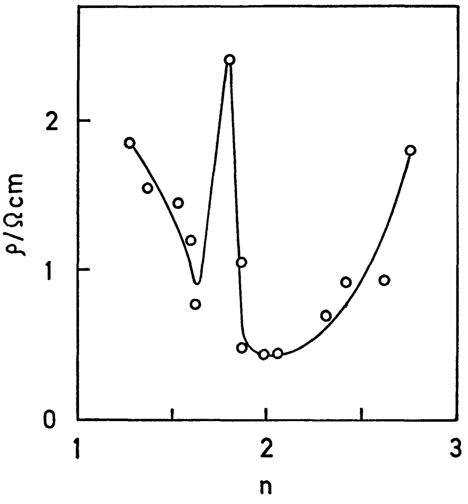


Fig. 13. Electrical resistivity at 20 °C plotted against the iodine content in the pyridazine–iodine system.

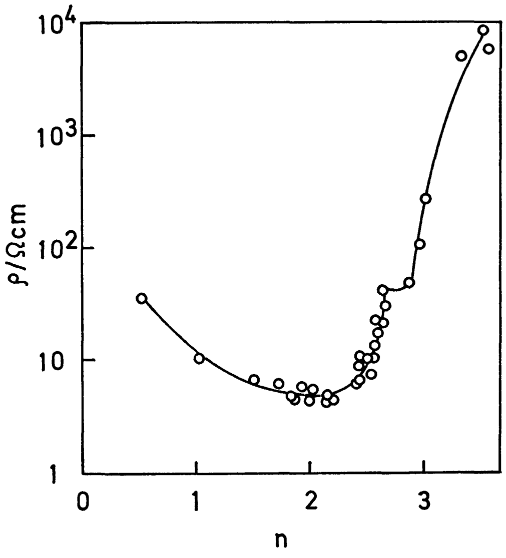


Fig. 14. Electrical resistivity at 20 °C plotted against the iodine content in the *N,N′*-diphenyl-*p*-phenylenediamine-iodine system.

of n=0.5—2.4, in accordance with the work by Hádek, and about 0.13 eV in the range of n=2.5—2.6. The change of the activation energy by lowering the temperature to about 0.22 eV in both the composition ranges was found around −20 °C, which is displaced by 30° above the temperature reported by Hádek.[19)]

Although the Seebeck coefficient at room temperature is negative regardless of the wide variation in composition, the whole range can be divided into three sections according to the magnitude and the temperature dependence: namely, $n<2.4$, n=2.4—2.9, and $n>3$. In the first range, the value is −20— −30 μV K^{-1} at room temperature and shows a minimum of about −60 μV K^{-1} near −70 °C. The change of the sign occurs at a lower temperature, the value at −130 °C (the lowest temperature examined) being about +90 μV K^{-1}. Thus, the relative contribution of electrons and holes to the conductivity seems to vary with the temperature. The second range cannot be distinguished from the first by the room-temperature value alone but the minimum is more negative and the value is about −50 μV K^{-1} even at −130 °C. The room-temperature value in the third range is significantly more negative, for example, about −200 μV K^{-1} at n=3.30. The low-temperature value is negative but vanishingly small, passing through a minimum of about −350 μV K^{-1} located around −20 °C. Thus, the compound appearing in the second composition range seems to be nonstoichiometric to some extent and its composition may be represented by (N,N'-diphenyl-p-phenylenediamine)$_5$I$_{13}$. Because of the relatively small change in resistivity around n=2, the resistivity-composition isotherm method fails to establish the ideal composition of the low-resistivity complex studied by Hádek *et al.* and also by Sano *et al.*

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