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The Electrical Properties of Iodine Complexes of *N*-Methyl- and *N*-Ethyl-phenothiazines and Their Mixtures

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The electrical resistivities and Seebeck coefficients of 2:3 iodine complexes of *N*-methyl- and *N*-ethyl-phenothiazines were measured. The former complex exhibits a resistivity of 2.0 ohm cm and an activation energy for semiconduction of 0.20 eV at 20°C. Applying the equation of Johnson and Lark-Horowitz for the Seebeck coefficient of an intrinsic semiconductor, the ratio of the electron mobility to the hole mobility in the *N*-methyl-phenothiazine complex was found to be 2.08 and the electron mobility was estimated as 0.23 cm²/Vsec. The resistivity of the *N*-ethylphenothiazine complex is 74 ohm cm, and the activation energy 0.15 eV at 20°C. In this complex, the hole appears to be more mobile by a factor of five than the electron. Lichtenecker's logarithmic rule is observed neither by the resistivity nor by the activation energy of the mixtures of these two complexes.

N-Methyl-phenothiazine has been found by one of the present authors to form a 2:3 iodine complex exhibiting an electrical resistivity as low as 1.4 ohm cm at room temperature.¹⁾ As this value is only about one-tenth of the resistivity shown by the iodine complex of the unsubstituted donor, it seemed that a further examination of the size effect of the alkyl group on the electrical properties would be interesting. A pre-

liminary study of this problem indicated an increase in the resistivity upon the introduction of larger alkyl groups.²⁾ However, the comparison made in that study was merely qualitative because no complexes with a definite composition were isolated. Here, we wish to report a comparison of the resistivities and Seebeck coefficients of 2:3 iodine complexes of *N*-methyl- and *N*-ethyl-phenothiazines in order to see how the introduction of a larger group modifies the properties.

According to Lichtenecker, a logarithmic rule ap-

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plies for the resistivity value when two non-interacting materials are mechanically mixed.³⁾ The essential expression derived by him is:

$$\rho_m = \rho_1^{1-x} \rho_2^x \quad (1)$$

where ρ_m is the resistivity of the mixture; ρ_1 and ρ_2 are the resistivities of the respective components, and x is the volume fraction of the second component. If the materials are semiconductors, we obtain:

$$\rho_m = \rho_{01}^{1-x} \rho_{02}^x \exp\{[(1-x)E_1 + xE_2]/kT\} \quad (2)$$

where ρ_{01} and ρ_{02} are preexponential factors of the components and where E_1 and E_2 are the respective activation energies for semiconduction. Recently, Ulbert has studied the electrical properties of mechanical mixtures of two chemically-stable organic semiconductors, 4,4'-bis(dimethylamino)-diphenylamine iodide and the iodine complex of *N,N'*-bis(aminophenyl)-*p*-phenylenediamine.⁴⁾ The generalized logarithmic rule, Eq. (2), has been well observed not only by the resistivity but also by the activation energy of the mixtures. Therefore, we examined the properties of the mixtures to see whether or not the same rule applies to the present iodine complexes.

Experimental

Materials. The *N*-alkyl-phenothiazines were prepared by the reaction of the corresponding alkyl iodide on phenothiazine following the procedure given by Bernthsen.⁵⁾ The complexes were precipitated by mixing the components dissolved in ether. As was described in our earlier paper, the complexes dissociate into their components when dissolved in benzene, so the compositions were determined by iodometric titration.¹⁾ For the examination of the (*N*-methyl- and *N*-ethyl-phenothiazines)-iodine, the weighed complexes were thoroughly mixed by grinding in an agate mortar. Samples with the following volume percents of the *N*-ethyl-phenothiazine complex were prepared: 13.5, 27.1, 44.7, 49.4, 58.2, and 72.6.

Measurements. The resistivities of compressed polycrystalline samples were measured by a potential probe method in the range from -90°C to room temperature. Below the lower limit, the contact between the pellet and the probe became too sluggish for any reliable measurements to be made. The pellet and its holder were accommodated in a thick copper cylinder and cooled with liquid nitrogen. When the temperature of the sample had been lowered enough, the whole was transferred into an empty Dewar and allowed to warm up slowly to room temperature. During this process, the temperature of the holder was recorded on the *X* axis of a Yokogawa X-Y recorder, Type 3078, and the potential drop between the probes and that in the standard resistance, on the *Y*₁ and *Y*₂ axes respectively.

The Seebeck voltage measurements were carried out on the same pellets as those employed for the resistivity measurements. In this mounting, the faces painted with colloidal graphite were clamped between copper electrodes. The temperatures on the upper and lower faces of the pellet were measured by means of copper-constantan thermocouples attached to the electrodes. The Seebeck coefficient observed with a dried colloidal graphite block was $1\text{--}3\ \mu\text{V}/\text{deg}$ over

the entire temperature range; therefore, no correction was made for the following data. The temperature difference between the two faces was not controlled except near room temperature; it ranged from 10 to 30°C . The limit of the measurable low temperature, the mean value of those temperatures at the two faces, was about -130°C . The measurements were made by recording the Seebeck voltage on the *X* axis and the thermocouple potentials on the *Y*₁ and *Y*₂ axes.

The densities of the complexes were determined from the pellets.

Results and Discussion

The complexes of *N*-methyl- and *N*-ethyl-phenothiazines consist of two molecules of thiazine and three of iodine. The former complex is black, and the latter dark green. They melt at 72° and 74.5°C respectively. In Fig. 1 the logarithm of the resistivity is plotted

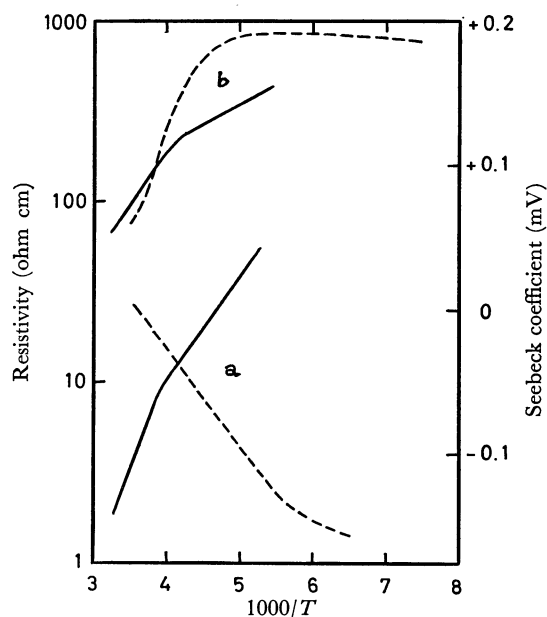


Fig. 1. Electrical resistivities (—) and Seebeck coefficients (---) of (a) *N*-methyl-phenothiazine-iodine and (b) *N*-ethylphenothiazine-iodine complexes.

against the reciprocal temperature. The plot gives two straight lines, with a break around -70°C in both cases. The activation energy for semiconduction, calculated on a basis of:

$$\rho = \rho_0 \exp(E/kT) \quad (3)$$

is 0.20 eV in the higher temperature region and 0.11 eV in the lower temperature region of the curve for the *N*-methyl-phenothiazine-iodine complex. In our earlier work, the activation energy was estimated as 0.14 eV by measurements over a rather narrow temperature range (from 0 to 40°C). This value must be compared with that of 0.20 eV obtained in the present work. The resistivity value at 20°C is 2.0 ohm cm; it is in reasonable agreement with the previously-reported one, 1.4 ohm cm. Similarly, 0.15 and 0.045 eV can be estimated for the *N*-ethyl-phenothiazine-iodine complex. The resistivities at 20°C and the activation energies at this temperature are summarized in Table

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TABLE 1. ELECTRICAL PROPERTIES OF THE IODINE COMPLEXES OF PHENOTHIAZINE AND ITS *N*-ALKYL DERIVATIVES IN THE HIGHER TEMPERATURE REGION

Substituent	ρ at 20°C (ohm cm)	E (eV)	μ_e/μ_h	m_e/m_h	Ref.
None	20	0.17	—	—	1
None	13	0.19	—	—	6
Methyl	1.4	0.14	—	—	1
Methyl	2.0	0.20	2.08	1/130	This work
Ethyl	74	0.15	1/5.0	530 ^{a)}	This work

a) By extrapolation of the Seebeck coefficient curve in the higher temperature region.

1. The values for the phenothiazine-iodine complex, taken from our previous papers are included for the sake of comparison.^{1,6)} The results clearly indicate that the methyl substitution makes the arrangement of thiazine molecules in the iodine complex the optimum for electrical conduction. When the size of the group on the nitrogen atom is either smaller or larger, the overlapping of the thiazine molecules appears to decrease, resulting in an increase in the resistivity. Effects of such a size have been noted in several works on anion-radical salts derived from tetracyanoquinodimethane and also those derived from tetrahalo-*p*-diphenylquinones.⁷⁻¹⁰⁾ It is interesting to note that, contrary to the iodine complexes, the 2,3-dichloro-5,6-dicyano-*p*-benzoquinone complex of *N*-methyl-phenothiazine was found to have a resistivity about ten times higher than that of unsubstituted phenothiazine.^{2,11)} A compensating relation between the activation energy and the logarithm of resistivity has been frequently pointed out when a series of compounds, such as a series of derivatives of a given compound, is examined.¹²⁻¹⁴⁾ From this standpoint, the present complexes are rather anomalous. The most conducting *N*-methylphenothiazine complex is found to exhibit the highest activation energy for semiconduction.

The temperature dependence of the Seebeck coefficient, Q , is also presented in Fig. 1. First of all, the change in the sign by the kind of alkyl group must be noted; that is, the coefficient of the *N*-methyl-phenothiazine complex is negative except near and above room temperature, while that of the *N*-ethyl-phenothiazine complex is positive over the whole measurable range. A further observation of the alternation of the sign by the substituent is provided by the experiment on the phenothiazine-iodine complex, the Seebeck coefficient of which is positive (about 0.15 mV/deg in the

vicinity of room temperature).¹⁵⁾ It must be added that the sign of the Seebeck coefficient in the phenothiazine-iodine system has been reported by Bhat and Rao to vary with the donor-acceptor ratio.¹⁶⁾ The following values, measured at 30°C, have been presented by them: +0.132 mV/deg at a composition of 1:3, -0.150 mV/deg at 1:1, and +0.300 mV/deg at 3:1. Unfortunately, none of the compositions mentioned here corresponds to the 2:3 stoichiometry reported by us and also by Gutmann and Keyzer.^{1,6,17)}

The higher-temperature region of the curve is practically straight and seems to fit in with the expression for the thermoelectric motive force of an intrinsic semiconductor:^{18,19)}

$$Q = -\frac{k}{e} \left[\frac{b-1}{b+1} \left(\frac{E_g}{2kT} + 2 \right) + \frac{3}{4} \ln \frac{m_e}{m_h} \right] \quad (4)$$

where E_g is the width of the forbidden band and where m_e and m_h are the effective masses of the electron and the hole respectively. In this equation, b denotes the ratio of the electron mobility, μ_e , to the hole mobility, μ_h ; it is given by:

$$b = \frac{\mu_e}{\mu_h} = \left[\frac{E_g}{2} - \frac{AQ}{\Delta(10^3/T)} \right] \left[\frac{E_g}{2} + \frac{AQ}{\Delta(10^3/T)} \right]^{-1} \quad (5)$$

provided that Q is measured in mV. The application of these two equations implies that we should accept the band model as a basic work hypothesis. In the case of the *N*-methyl-phenothiazine complex, b is evaluated as 2.08, assuming that $E_g/2 = 0.20$ eV. As is shown in Fig. 1, the change of the sign is observed at $10^3/T = 3.60$. Therefore, m_e/m_h can be estimated to be about 130 by means of Eq. (4). The values obtained for the *N*-ethyl-phenothiazine complex are listed in Table 1. The conductivity, σ , is given by:

$$\sigma = \frac{1}{\rho} = e(\mu_e + \mu_h)N \exp(-E/kT) = e\mu_e \left(\frac{b+1}{b} \right) N \exp(-E/kT) \quad (6)$$

where $N = 2.53 \times 10^{22}$ *N*-methyl-phenothiazine molecules or 2.30×10^{22} *N*-ethyl-phenothiazine molecules per cm³ of the complex. With the values given in Table 1, the electron mobility in the *N*-methyl-phenothiazine complex is estimated as 0.23 cm²/Vsec. This value falls right on the borderline between the band and hopping conduction and is of the same order as the only known Hall mobility observed with iodine complexes.²⁰⁾ On the other hand, the hole mobility in the *N*-ethyl-phenothiazine complex is estimated to be smaller by a factor of hundreds. The width of a forbidden band is expected to reflect the strength of the interactions amongst the molecular orbitals; this strength, in turn, depends upon the degree of overlap of the orbitals. When the overlap is poor, the band is narrow

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and the carrier mobility is low. Consequently, both the small activation energy and the high resistivity observed in the *N*-ethyl-phenothiazine complex may be attributed to the poor overlapping of the thiazine molecules.

The slope of the Seebeck coefficient curve of the *N*-methylphenothiazine complex gradually becomes smaller in the temperature region which is markedly lower than the break observed in the resistivity curve. In the lower temperature region, the complex may be considered as an extrinsic semiconductor. The Seebeck coefficient may be expressed by:

$$Q = \pm \frac{k}{e} \left\{ 2 + \ln \left[2 \left(\frac{2\pi m^* kT}{h^2} \right)^{3/2} \right] - \ln c \right\} \quad (7)$$

where c is the concentration of the free electron or the hole, depending upon which is the major carrier and where m^* is the effective mass of the carrier. If kT is relatively small compared with the energy difference, ΔE , between an impurity level and the edge of the conduction or valence band, Q can be approximated by:

$$Q = \pm \frac{k}{e} \left[C + \frac{3}{2} \ln(kT) + \Delta E/2kT \right] \quad (8)$$

where C represents all the terms independent of the temperature. This expression is for a semiconductor with a partially-ionized impurity level. The $(3/2) \ln(kT)$ and $\Delta E/2kT$ terms vary in the opposite direction with respect to the temperature. As was pointed out by Hadek and Ulbert, a relatively good compensation between these two terms can be expected when the activation energy, $\Delta E/2$, is about 0.02 eV.²¹⁾ If we assume that the activation energy estimated by the resistivity measurement in the lower temperature region is valid even in the lower temperature region of the Seebeck coefficient curve, the change due to the former term can be expected to be overbalanced by that due to the latter, in accordance with the observations. However, the agreement is only qualitative. For example, the slope in the unit of $\Delta Q/\Delta(10^3/T)$ is calculated by Eq. (8) to be about 0.08 mV if $\Delta E/2 = 0.11$ eV. This value cannot be differentiated from the slope found in the higher temperature region. Unless the change in the activation energy occurs below the lower limit of the resistivity measurement, the observed slope is in serious disagreement with the calculated one. In the case of the *N*-ethyl-phenothiazine complex, the changes in the slope of the Seebeck coefficient curve are found around -15 and -50°C ($10^3/T = 3.9$ and 4.5). None of them is located close to the break in the resistivity curve. The observed slope in the intermediate temperature region, 0.18 mV, is appreciably higher than that given by Eq. (8) with $\Delta E/2 = 0.045$ eV. Thus, it appears to be difficult to explain the Seebeck coefficient in the lower temperature region by the band model. This conclusion is not surprising if we consider the values of the carrier mobilities estimated above.

The resistivity-composition isotherms at $10^3/T = 3.5$ and 4.5 , where the component complexes may be supposed to behave as intrinsic and extrinsic semiconductors

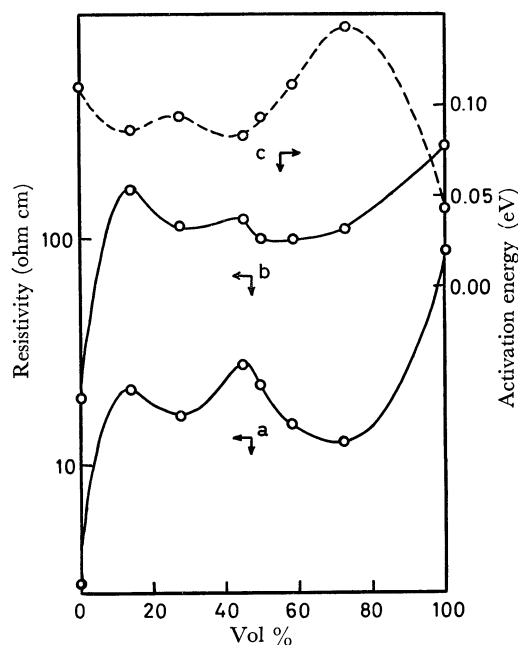


Fig. 2. Resistivities at (a) $10^3/T = 3.5$ and (b) $10^3/T = 4.5$ and (c) activation energies for semiconduction in the lower temperature region determined for the mixtures of iodine complexes of *N*-methyl- and *N*-ethyl-phenothiazines.

respectively, are presented in Fig. 2. Clearly, the present system does not obey Lichtenecker's logarithmic rule. The resistivity of the mixture at room temperature is much higher than that given by Eq. (1) when the volume percent of the *N*-ethyl-phenothiazine complex is less than 50%, and much lower when the percent is higher than 50%. In other words, the resistivity of the component complex is much more sensitive to the addition of a small amount of the other one than one would expect from Eq. (1). The resistivity exhibits a rather complicated temperature-dependence near room temperature; therefore, the relationship between the activation energy and the composition cannot be obtained.

When the temperature is lowered below -20°C ($10^3/T = 4.0$), straight lines are obtained in the resistivity curve of all the mixtures. The isotherm at $10^3/T = 4.5$ bears some resemblance to that observed in the higher temperature region. The deviation from Eq. (1) is small when the percent of the *N*-ethyl-phenothiazine complex is high; however, such a coincidence is accidental. As is plotted in Fig. 2, the activation energy does not obey Eq. (2), but depends, in a complicated way, on the composition. A marked maximum in the activation energy is found around 75% (see Curve c in Fig. 2); therefore, the resistivity-composition isotherm gives a large positive deviation from Eq. (1) in the entire composition if measured below -70°C ($10^3/T = 5.0$). As a result, an increase in the resistivity of the *N*-ethyl-phenothiazine complex by the addition of a small amount of the *N*-methyl-phenothiazine complex is observed in such a temperature range. In addition, it must be noted that the shallow minimum around 30% in the resistivity-composition isotherm becomes less pronounced upon cooling. This change arises partially from the shift of the minimum at a

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higher content of the *N*-ethylphenothiazine complex to about 50%. The remarkable difference in the electrical properties between Ulbert's mixed system and ours must be attributed to the interaction of the two complexes in the latter system. As the room temperature is as high as $0.85 T_m$, where T_m is the melting point

given in °K, it is very likely that mixing results in the mutual, possibly partial, dissolution of the complexes.

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