A Solid-state Electrochemical Study on the Phenothiazine–Iodine and Related Complexes

Toshiyuki MATSUMOTO and Yoshio MATSUNAGA*

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received May 30, 1980)

The electromotive force (emf) of a solid-state galvanic cell, Ag|AgI|PT–I_n, where PT–I_n is the phenothiazine–iodine complex, was examined as functions of the composition, n, and also of the temperature. Below n=2.5, a value of 616 mV was obtained at 25 °C. The emf increases stepwise to 620 mV at n=2.5 in conformity with the formation of a complex cation radical pentaiodide, as established by our earlier work. A continuous increase up to 649 mV was found before n=3, indicating the appearance of a nonstoichiometric phase covering the range from n=2.8 to 3. The upper limit of the existence region exactly corresponds with the minimum in the resistivity-composition isotherm. Similar studies with benzo[*a*]- and benzo[*c*]phenothiazines revealed the formation of three or four distinct nonstoichiometric complexes in each system. The Gibbs energy, enthalpy, and entropy of cell reactions and complex formation reactions are presented. The stability of the iodine complexes was found in the following order: benzo[*a*]phenothiazine>benzo[*c*]phenothiazine>phenothiazine.

The phenothiazine–iodine complex (PT–I_n) has been known as a semiconducting material with a relatively low electrical resistivity.[1] The vibrational spectrum of the complex at n=3, where the minimum resistivity is obtainable, has been shown to be distinctly different from that of the parent organic compound but nearly identical with that of the cation radical bromide prepared by the method of Kehrmann and Diserens.[2] Our subsequent studies have distinguished two vibrational patterns for the bromide samples,[3] and established the existence of both the simple and complex bromides.[4] The spectrum of the iodine complex is in accordance with that of the complex bromide where the two thiazine molecules share a unit positive charge and are equivalent in the time scale of infrared spectroscopy. This conclusion is in conflict with the fact that six atoms of iodine per $(\text{phenothiazine})_2^+$ ion do not fit to the composition of any polyiodide. We have also examined the electrical properties as a function of the composition.[5] Such a study has showed that the resistivity-composition isotherm measured with polycrystalline compactions consists of three portions of smooth curves. A sharp edge is located at n= 2.5, the value at room temperature being about 800 Ω cm. At the same composition, 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 have been noted. These results clearly indicate the formation of a complex cation radical salt, $(\text{phenothiazine})_2^+I_5^-$, and resolve, at least in part, the above-mentioned conflict. By further addition of iodine, the resistivity reaches a minimum of about 20 Ω cm at n=3 and then increases rapidly. The drastic decrease between n=2.5 and 3 was attributed to the charge carriers generated by the incorporation of extra iodine into the complex cation radical pentaiodide. However, the exact form of the incorporated iodine remains to be clarified.

Undoubtedly the careful examination of the electrical properties as functions of the composition could have served as a powerful tool available for elucidating the constitution of semiconducting phenothiazine–iodine complex. Nevertheless, we are not certain that the observed edge is indicative of the formation of a stoichiometric complex or of the ideal composition of a nonstoichiometric one. As to the resistivity minimum, it may represent the composition of a stoichiometric complex or the limit of the deviation from n=2.5 or some other stoichiometry. Moreover, the formation of other complexes which do not show significant anomalies in the isotherm cannot be ruled out. Consequently, it seemed desirable to examine the other physical quantity which depends on the composition quite differently from the electronic properties studied before. Of particular interest for this purpose are experiments on solid-state galvanic cells, as two-phase mixtures should be identified by constant electromotive force (emf), a stoichiometric complex by a discontinuous increase and a nonstoichiometric single-phase region by a continuous increase in emf with n.

Gutmann *et al.* were the first to explore solid-state galvanic cells using the electronically-conducting iodine complexes as cathodes.[6] The development of similar cells consisting of AgI-based solid electrolyte and the perylene–iodine complex has been described by Louzos *et al.*[7] Furthermore, Pampallona *et al.* have shown that iodine electrodes based on phenothiazine and its *N*-methyl derivative offer excellent prospects as practical cathodes.[8] Aside from such applied research results, attempts to determine the thermodynamic formation values for some solid iodine complexes have been made by measuring the emf of solid-state cells by Aronson *et al.* and also by McKechnie *et al.*[9,10] The complexes studied by the latter group include the phenothiazine–iodine (n=3).

Experimental

Materials. The phenothiazine was commercially obtained and purified by recrystallization and then by sublimation in a vacuum. The benzo[*a*]- and benzo[*c*]phenothiazines were prepared by the reaction of sulfur on *N*-phenyl-1- and -2-naphthylamines respectively, using a small amount of iodine as the catalyst.[11] The former thiazine was purified by recrystallization from ligroine, mp 135—136 °C. The melting point of the latter after recrystallization was found to be 177 °C, in agreement with the value reported by Knoevenagel, 176 °C;[11] however, this value was raised to 185 °C by sublimation in a vacuum. The complexes were obtained by careful grinding of the weighed

thiazine and iodine in an agate mortar in the presence of a small amount of benzene. The samples thus prepared were heated to 80 °C in a short time to complete the reaction and also to remove all traces of the solvent. The iodine contents were determined by microanalysis.

Measurements. The galvanic cell, Ag|AgI|thiazine–iodine complex (T–I_n), was assembled in the following way. A cylindrical block of Teflon with a 1-cm-diameter hole was placed on a piece of platinum plate fixed on a brass block. Silver powder and then silver iodide powder were pressed inside the Teflon cylinder. An 8-mm-diameter compaction of the iodine complex was made and was placed on the flat surface of the silver iodide. The upper surface of the compaction accommodated in the Teflon cylinder was covered with another piece of platinum plate fixed on a 1-cm-diameter brass rod with a rim, which was fitted into the hole of the second cylindrical block of Teflon. The cell placed between the two platinum electrodes was tightened employing three pairs of bolts and nuts applied to the brass block and the second block of Teflon, so that the iodine complex compaction made good contact with the silver iodide layer. Platinum leads provided electrical contact to the electrodes. The whole assembly, with a diameter of 3 cm and a height of less than 4 cm, was placed in a glass tube and dipped into an oil-bath. The temperature was regulated between room temperature and 80 °C with an accuracy better than ±0.25 °C. The emf was measured by means of a high-impedance ($\approx 10^{10}\,\Omega$) universal digital meter, Yokogawa 2502. For the readings of emf, the cell was kept at each temperature for about one hour. The measurements were made only while the temperature was increased and were repeated until steady, reproducible emf data could be attained. The emf was a linear function of the temperature in most of the examined temperature range. When the emf near room temperature deviated from the expected linear relationship, the value at 25 °C was estimated by the extrapolation of the high-temperature data.

Results and Discussion

Phenothiazine–Iodine. The emf increases linearly by raising the temperature. For example, the data at n=1.10 and 3.01 are presented in Fig. 1. The open and shaded circles indicate the values measured by different runs on the same cell. They are expressed by E/mV=616+0.300(t−25), and by E/mV=649+0.230(t−25) respectively.

The compositional variation of the emf at 25 °C is shown in Fig. 2. Below n=2.5, the cell maintains an emf of 616 mV. Attempts to obtain steady, reproducible emf with the complexes below n=0.5 were unsuccessful, probably because of the high electrical resistivity of the complex.[5] As the vibrational spectrum of a sample at n=0.65 clearly shows the coexistence of free phenothiazine, the samples below n=2.5 may be mixtures of the parent organic compound and its iodine complex (n=2.5). In our previous work, we tried to prepare "monoiodide" by the reaction of hydroiodic acid with an equimolar mixture of phenothiazine and its *S*-oxide and obtained a product which is approximately expressed by PT–$I_{1.35}$.[5] It now seems probable that the "monoiodide" does not exist in this system.

The emf increases stepwise at n=2.5, indicating

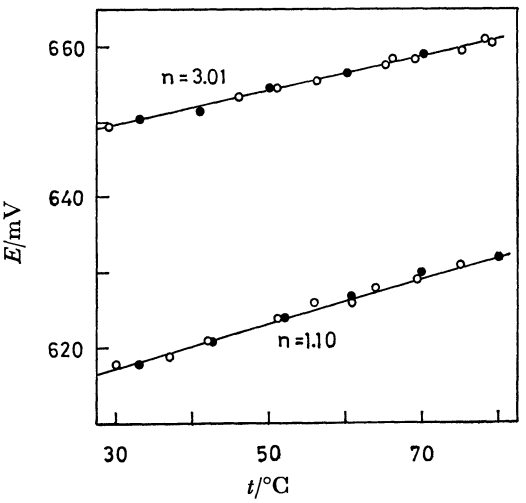

Fig. 1. Electromotive force of the solid-state cells, Ag|AgI|phenothiazine–iodine (PT–I_n).

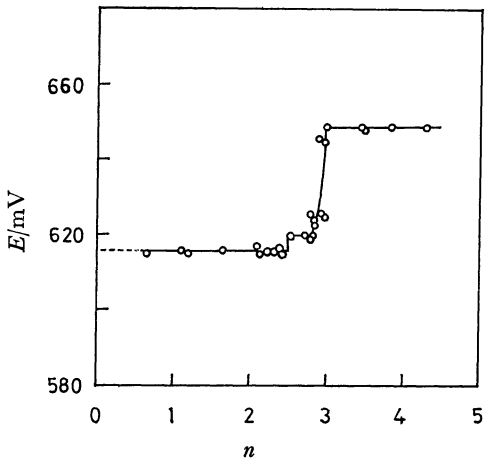

Fig. 2. Electromotive force of the solid-state cell, Ag|AgI|phenothiazine–iodine (PT–I_n) *versus* n at 25 °C.

that the complex is stoichiometric. This composition corresponds exactly to the edge appearing in the resistivity-composition isotherm. The two solid phases are involved in the composition range from n=2.5 to 2.8. Then, a continuous increase observed between n=2.8 and 3.0 implies that the complex is homogeneous over this range. In other words, a nonstoichiometric complex is formed. Although the lower limit of the region of existence was not detected by the resistivity-composition isotherm, the upper limit is in accordance with the composition of a deep minimum. Pampallona *et al.* have reported an emf of 630 mV for the cell Ag, $RbAg_4I_5$|$RbAg_4I_5$|PT–I_3,[8] and also McKechnie *et al.* have obtained 646 mV with the cell, Ag|AgI|PT–I_3.[10] These values are lower than ours at n=3; however, small deviations of n from 3 may easily give rise the observed differences. Both the reported values fit into the emf range of the nonstoichiometric complex.

A plateau indicative of a two-phase region appears above n=3, giving an emf of 649 mV. As this value is markedly lower than 688.3 mV reported by McKechnie *et al.* for the cell reaction, Ag(s)+1/2I_2(s)→AgI(s), another complex with n>4.3 must exist in

the present system. We noted before that the vibrational spectrum of phenothiazine mixed with a large amount of iodine is different from that of the complex at $n=3$, but essentially identical with that of the simple cation radical bromide;[5] therefore, the expected complex may be some kind of simple polyiodide. No attempt was made to determine its composition by the present technique, because of the high vapor pressure of iodine and also of the high electrical resistivity.

Since only silver ions migrate in AgI, the emf values observed in the two-phase regions below $n=2.5$ and between $n=2.5$ and 2.8 are determined by the following virtual cell reactions:

$$Ag + 1/2.5\,PT\text{-}I_{2.5} \longrightarrow AgI + 1/2.5\,PT$$

and

$$Ag + 1/0.3\,PT\text{-}I_{2.8} \longrightarrow AgI + 1/0.3\,PT\text{-}I_{2.5}.$$

If the Gibbs energies are calculated in terms of the reactions,

$$2.5\,Ag + PT\text{-}I_{2.5} \longrightarrow 2.5\,AgI + PT \quad (1)$$

and

$$0.3\,Ag + PT\text{-}I_{2.8} \longrightarrow 0.3\,AgI + PT\text{-}I_{2.5}, \quad (2)$$

they are -148.5 and -17.9 kJ mol^{-1} (of the complex). These values represent the area under the emf composition curve between the upper and lower limits of n defined in each cell reaction.[12] Consequently, the Gibbs energy for the cell reaction to which the nonstoichiometric complexes with $n=2.8$ and 3 par-

$$0.2\,Ag + PT\text{-}I_3 \longrightarrow 0.2\,AgI + PT\text{-}I_{2.8} \quad (3)$$

ticipate, may be estimated by a graphic method to be -12.3 kJ mol^{-1} (of the complex). Combining with $\Delta G_f^\circ(AgI) = -66.4$ kJ mol^{-1},[10] the Gibbs energies in terms of the complex formation reactions,

$$PT + 2.5/2\,I_2 \longrightarrow PT\text{-}I_{2.5},$$

$$PT + 2.8/2\,I_2 \longrightarrow PT\text{-}I_{2.8},$$

and

$$PT + 3/2\,I_2 \longrightarrow PT\text{-}I_3$$

are determined to be -17.5, -19.5, and -20.5 kJ mol^{-1} respectively. McKechnie *et al.* have assumed that the reaction occurring in their cell is

$$Ag + 1/3\,PT\text{-}I_3 \longrightarrow AgI + 1/3\,PT,$$

and computed the ΔG value of -62.3 kJ mol^{-1} (of Ag). As the assumed reaction is not correct, their Gibbs energy of the complex formation, -12.3 kJ mol^{-1} (of the complex), is appreciable smaller than ours.

The slope of the emf *versus* the temperature graph shows considerable scatter and differs up to 15% from the mean value; this is shown in Fig. 3. The entropy changes for the cell reactions (1), (2), and (3) are estimated to be 73.5 ± 1.3, 8.8 ± 0.2, and 4.4 ± 0.1 J K^{-1} mol^{-1}. The application of Gibbs-Helmholtz equation yields enthalpies of -126.6 ± 0.4, -15.3 ± 0.04, and -11.0 ± 0.03 kJ mol^{-1} for these cell reactions. With the aid of $\Delta S_f^\circ(AgI) = 13.4\pm0.1$ J K^{-1} mol^{-1},[10] the entropy changes in terms of the complex formation reactions can be computed to be -40.0 ± 1.5, -44.8 ± 1.7, and -46.5 ± 1.8 J K^{-1} mol^{-1}, and

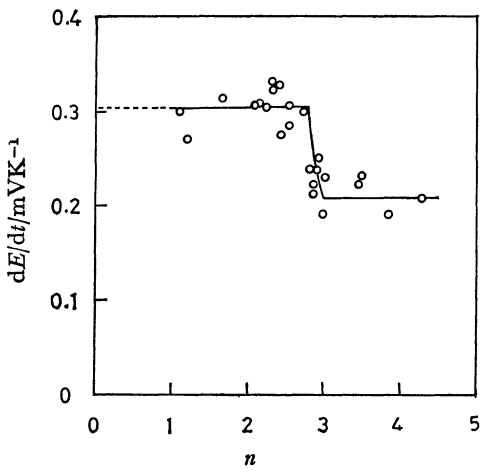

Fig. 3. Temperature coefficient of electromotive force of the solid-state cell, Ag|AgI|phenothiazine-iodine ($PT\text{-}I_n$) versus n.

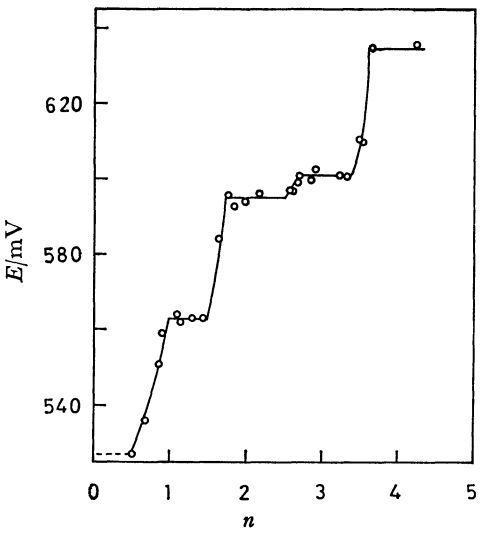

Fig. 4. Electromotive force of the solid-state cell, Ag|AgI|benzo[*a*]phenothiazine-iodine ($B[a]PT\text{-}I_n$) *versus* n at 25 °C.

with $\Delta H_f^\circ(AgI) = -62.4$ kJ mol^{-1}, the enthalpy changes are found to be -29.4 ± 0.5, -32.8 ± 0.5, and -34.3 ± 0.5 kJ mol^{-1}. It must be added that the temperature coefficient of the emf at and above $n=3$ is twice as large as that reported by McKechnie *et al.*, 0.114 mV K^{-1}, for unknown reasons. Since their coefficient is less than that for the cell reaction, Ag(s)+1/2 I_2(s)→AgI(s), the entropy change for the complex formation reported by them is positive and the magnitude is smaller by a factor of one-tenth.

Benzo[a]*phenothiazine–Iodine.* The results presented in Fig. 4 clearly indicate the formation of four distinct complexes, $B[a]PT\text{-}I_n$, in the examined composition range. The interesting feature of this system is the nonstoichiometry in all the phases. The first phase appears at and below $n=1$, the second, between $n=1.5$ and 1.7, the third, between $n=2.5$ and 2.7, and the fourth, between $n=3.4$ and 3.6. The two-phase region appearing between $n=1$ and 1.5 exhibits an emf of 563 mV; the region between

Table 1. Thermodynamic data for the cell reaction, $\Delta n\,Ag + T\text{-}I_n \longrightarrow \Delta n\,AgI + T\text{-}I_{n-\Delta n}$

Eq.	n	Δn	E/mV	ΔG/kJ mol^{-1}	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
			Phenothiazine-Iodine complexes			
1	2.5	2.5	616	−148.5	−126.6±0.4	73.5±1.3
2	2.8	0.3	620	−17.9	−15.3±0.04	8.8±0.2
3	3.0	0.2	a)	−12.3	−11.0±0.03	4.4±0.1
			Benzo[*a*]phenothiazine-Iodine complexes			
4	0.5	0.5	527	−25.4	−13.9±0.7	38.6±2.4
5	1.0	0.5	a)	−26.2	−18.3±0.7	26.5±2.4
6	1.5	0.5	563	−27.2	−22.6±0.3	15.4±1.0
7	1.7	0.2	a)	−11.2	−9.4±0.2	6.2±0.4
8	2.5	0.8	595	−45.9	−38.5±0.4	24.7±1.6
9	2.7	0.2	a)	−11.6	−10.0±0.04	5.3±0.2
10	3.4	0.7	601	−40.6	−35.9±0.1	15.8±0.2
11	3.6	0.2	a)	−12.0	—	—
			Benzo[*c*]phenothiazine-Iodine complexes			
12	0.5	0.5	550	−26.5	−23.3±0.2	10.6±0.5
13	1.0	0.5	a)	−27.0	−23.8±0.2	10.6±0.5
14	2.3	1.3	614	−77.0	−68.8±0.4	27.6±1.3
15	2.5	0.2	a)	−11.9	−10.6±0.1	4.2±0.2
16	3.0	0.5	616	−29.7	−26.5±0.2	10.6±0.5
17	3.5	0.5	a)	−30.4	—	—

a) One-phase region.

n=1.7 and 2.5, 595 mV; the region between n=2.7 and 3.4, 601 mV; and the region above n=3.6, 635 mV. Earlier, one of the present authors attempted the preparation of "monoiodide" and succeeded in isolating a product whose composition almost agrees with the ideal one.[13] Now it is certain that the monoiodide is formed in this system at the higher extreme of the existence region of a nonstoichiometric complex. On the other hand, the existence of the complex with n=3 studied earlier is not supported by the present work.[14] The resistivity-composition isotherm exhibits a sharp maximum at n=2.5 and broad minima which may be located anywhere near n=2 and 3. The composition at the resistivity maximum is the lower extreme of the third phase, possibly representing the ideal composition. The resistivity minimum located below n=2.5 is now identified as the upper limit of the existence region of the second phase (n=1.7) and that located above n=2.5 must be the lower limit of the existence region of the fourth phase (n=3.4). The complex at the former minimum may be regarded as $(B[a]PT)_2{}^+I_3{}^-$ containing an excess of iodine, and the complex at the latter as $(B[a]PT)_2{}^+I_7{}^-$ containing an excess of the thiazine.

The Gibbs energies are to be determined for the following eight cell reactions:

$$0.5\,Ag + B[a]PT\text{-}I_{0.5} \longrightarrow 0.5\,AgI + B[a]PT \quad (4)$$

$$0.5\,Ag + B[a]PT\text{-}I \longrightarrow 0.5\,AgI + B[a]PT\text{-}I_{0.5} \quad (5)$$

$$0.5\,Ag + B[a]PT\text{-}I_{1.5} \longrightarrow 0.5\,AgI + B[a]PT\text{-}I \quad (6)$$

$$0.2\,Ag + B[a]PT\text{-}I_{1.7} \longrightarrow 0.2\,AgI + B[a]PT\text{-}I_{1.5} \quad (7)$$

$$0.8\,Ag + B[a]PT\text{-}I_{2.5} \longrightarrow 0.8\,AgI + B[a]PT\text{-}I_{1.7} \quad (8)$$

$$0.2\,Ag + B[a]PT\text{-}I_{2.7} \longrightarrow 0.2\,AgI + B[a]PT\text{-}I_{2.5} \quad (9)$$

$$0.7\,Ag + B[a]PT\text{-}I_{3.4} \longrightarrow 0.7\,AgI + B[a]PT\text{-}I_{2.7} \quad (10)$$

$$0.2\,Ag + B[a]PT\text{-}I_{3.6} \longrightarrow 0.2\,AgI + B[a]PT\text{-}I_{3.4}. \quad (11)$$

We failed to obtain steady reproducible emf values for the cell reaction (4). As none of the known existence regions of the nonstoichiometric complexes is wider than 0.5 in the present system, we tentatively assumed the appearance of a two-phase region below n=0.5 where one of the phases is the parent organic compound. The computed Gibbs energies are summarized in Table 1. The Gibbs energy of complex formation and the value per iodine atom are given in Table 2. The latter value becomes less negative as more iodine is combined with benzo[*a*]phenothiazine. It must be emphasized that the benzo[*a*]phenothiazine complexes are far more stable than the phenothiazine complexes are. For example, the Gibbs energy divided by the number of iodine atoms at n=2.5 is −12.0 kJ mol^{-1} for the former complex, while the corresponding value is −7.0 kJ mol^{-1} for the latter.

As there are so many phases in this system, our data are insufficient to assign a temperature coefficient to each one. The coefficient decreases from about 0.8 mV K^{-1} at n=0.5 to 0.3 mV K^{-1} at n=1, and then maintains roughly the latter value (0.32±0.02 mV K^{-1}) up to n=2.5. Between n=2.7 and 3.4, the cells show a steady value of 0.234±0.005 mV K^{-1}. Because of the lack of data for the cell reaction (4) and also the inaccurate data for the other reactions, the probable errors of ΔH and ΔS values of the complex formation reactions are, much larger than those for the phenothiazine–iodine complexes (see Table 2).

Benzo[c]*phenothiazine–Iodine.* The emf *versus* the composition graph indicates the formation of three nonstoichiometric complexes, B[*c*]PT–I_n, in the studied range (see Fig. 5). The first complex covers the range from n=0.5 to 1, the second, n=2.3 to 2.5, and the third, n=3.0 to 3.5. The emf is 614 mV in the two-phase region between n=1 and 2.3, 616 mV be-

TABLE 2. THERMODYNAMIC DATA FOR THE COMPLEX FORMATION REACTION, $T+n/2\,I_2 \longrightarrow T\text{-}I_n$

n	ΔG/kJ mol^{-1}	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	$\Delta G \div n$/kJ mol^{-1}
		Phenothiazine-Iodine complexes		
2.5	−17.5	−29.4±0.5	−40.0±1.5	−7.0
2.8	−19.2	−32.8±0.5	−44.8±1.7	−6.9
3.0	−20.5	−34.3±0.5	−46.5±1.8	−6.8
		Benzo[*a*]phenothiazine-Iodine complexes		
0.5	−7.8	−17.3±0.7	−31.9±2.4	−15.6
1.0	−14.8	−25.8±1.4	−51.7±4.8	−14.8
1.5	−20.8	−34.4±1.7	−60.4±5.8	−13.9
1.7	−22.9	−37.5±1.9	−63.9±6.2	−13.5
2.5	−30.1	−48.9±2.3	−77.9±7.8	−12.0
2.7	−31.8	−51.4±2.3	−80.5±8.0	−11.8
3.4	−37.7	−59.2±2.4	−86.9±8.2	−11.1
3.6	−38.9	—	—	−10.8
		Benzo[*c*]phenothiazine-Iodine complexes		
0.5	−6.7	−7.9±0.2	−3.9±0.5	−13.4
1.0	−12.9	−15.3±0.3	−7.8±1.0	−12.9
2.3	−22.2	−27.6±0.7	−18.0±2.3	−9.7
2.5	−23.6	−29.5±0.8	−19.5±2.5	−9.4
3.0	−27.1	−34.2±1.0	−23.4±3.0	−9.0
3.5	−29.9	—	—	−8.5

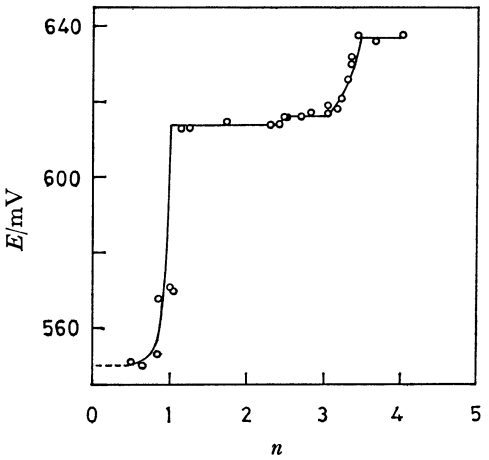

Fig. 5. Electromotive force of the solid-state cell, Ag|AgI|benzo[*c*]phenothiazine-iodine (B[*c*]PT-I_n) *versus* n at 25 °C.

tween n=2.5 and 3.0, and 637 mV above n=3. The "monoiodide" isolated in our previous work does exist in this system at the upper limit of a single phase region. Furthermore, the existence of the complex with n=3 is also firmly established by the emf data. The resistivity-composition isotherm shows an edge at n=2.5 and a broad minimum around n=2. The emf data strongly suggest that the minimum is located at n=2.3. The complex at this composition is the lower limit of a nonstoichiometric complex, the ideal composition of which is $(B[c]PT)_2{}^+I_5{}^-$.

The following six cell reactions are conceivable:

$$0.5\,Ag + B[c]PT\text{-}I_{0.5} \longrightarrow 0.5\,AgI + B[c]PT \quad (12)$$

$$0.5\,Ag + B[c]PT\text{-}I \longrightarrow 0.5\,AgI + B[c]PT\text{-}I_{0.5} \quad (13)$$

$$1.3\,Ag + B[c]PT\text{-}I_{2.3} \longrightarrow 1.3\,AgI + B[c]PT\text{-}I \quad (14)$$

$$0.2\,Ag + B[c]PT\text{-}I_{2.5} \longrightarrow 0.2\,AgI + B[c]PT\text{-}I_{2.3} \quad (15)$$

$$0.5\,Ag + B[c]PT\text{-}I_3 \longrightarrow 0.5\,AgI + B[c]PT\text{-}I_{2.5} \quad (16)$$

$$0.5\,Ag + B[c]PT\text{-}I_{3.5} \longrightarrow 0.5\,AgI + B[c]PT\text{-}I_3. \quad (17)$$

In this system too, we assumed that the samples with n<0.5 contain the free parent organic compound. The Gibbs energies computed for the cell reactions and the complex formation reactions are presented in Tables 1 and 2 respectively. The stabilities of these complexes are intermediate between those of the respective benzo[*a*]phenothiazine and phenothiazine complexes, the Gibbs energy divided by the number of iodine atoms at n=2.5 being −9.4 kJ mol^{-1}.

The temperature coefficients of the emf for Eqs. 12—16 are not distinguishable from each other; therefore, the average value of 0.22±0.01 mV K^{-1} was employed in the whole composition range below n=3. Above this limit, the coefficient decreases by a factor of a half by n=3.5. It must be noted that the ΔS values of the complex formation reactions for these three thiazines are so different that the value at n=2.5 in the benzo[*c*]phenothiazine complex is about a half of that in the phenothiazine complex, which in turn is about a half of that in the benzo[*a*]phenothiazine complex. As mentioned above, the ΔG values of the complex formation reactions for benzo[*c*]phenothiazine are considerably larger than those for phenothiazine; nevertheless, the ΔH values for these two thiazines are almost identical. In conclusion, the solid-state electrochemical study on these thiazine-iodine complexes has been able to determine clearly a number of phases which are often nonstoichiometric. We believe that the present technique deserves more attention in the investigation of electronically-conducting iodine complexes.

This work was partly supported by two Grants-in-Aid for Scientific Research Nos. 234028 and 434023 from the Ministry of Education, Science and Culture.

References

1) Y. Matsunaga, *Helv. Phys. Acta*, **36**, 800 (1963).
2) F. Kehrmann and L. Diserens, *Ber.*, **48**, 318 (1915).
3) Y. Matsunaga and K. Shono, *Bull. Chem. Soc. Jpn.*, **43**, 2007 (1970).
4) S. Doi and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **48**, 3747 (1975).
5) S. Doi, T. Inabe, and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **50**, 837 (1977).
6) F. Gutmann, A. M. Hermann, and A. Rembaum, *J. Electrochem. Soc.*, **114**, 323 (1967).
7) D. V. Louzos, W. G. Darland, and G. W. Mellors, *J. Electrochem. Soc.*, **120**, 1151 (1973).
8) M. Pampallona, A. Ricci, B. Scrosati, and C. A. Vincent, *J. Appl. Electrochem.*, **6**, 269 (1976).
9) S. Aronson, G. Sinensky, Y. Langsam, and M. Binder, *J. Inorg. Nucl. Chem.*, **38**, 407 (1976).
10) J. S. McKechnie, L. D. S. Turner, and C. A. Vincent, *J. Chem. Thermodyn.*, **1979**, 1189.
11) E. Knoevenagel, *J. Prakt. Chem.*, **89**, 1 (1914).
12) A. S. Nagelberg and W. L. Worrell, *J. Solid State Chem.*, **29**, 345 (1979).
13) Y. Matsunaga and Y. Suzuki, *Bull. Chem. Soc. Jpn.*, **46**, 719 (1973).
14) Y. Matsunaga and Y. Suzuki, *Bull. Chem. Soc. Jpn.*, **45**, 3375 (1972).