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A Solid State Electrochemical Study on the 5,6 : 11,12-Bis(epidithio)-naphthacene–Iodine and Bromine Complexes

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Electromotive force (emf) measurements were made on solid-state galvanic cells, Ag|AgI|TTT–I_n, where TTT–I_n is the 5,6:11,12-bis(epidithio)naphthacene–iodine complex, as functions of the composition, n, and also of the temperature. A continuous increase in the emf at 25 °C from 491 to 593 mV was observed in the range from $n=1.0$ to 1.5, suggesting the occurrence of a nonstoichiometric phase. The upper limit of the existence region agrees with the composition of the well-known metallic phase. The emf changes again continuously up to 628 mV in the range from $n=2.7$ to 2.9, which corresponds with the composition of another highly-conducting complex. Similar measurements were carried out for the cells Ag|AgBr|TTT–Br_n. Distinct phases were found at the following compositions: $n=0.5$—0.8, about 1, about 1.2, about 1.5, and about 2. The Gibbs energy, enthalpy, and entropy of cell reactions as well as complex formation reactions were estimated.

Mixed-valence 5,6:11,12-bis(epidithio)naphthacene–iodine complexes, TTT–I_n,[1] have attracted the interest of many research groups. The complex TTT–$I_{1.5}$ is among the extensively studied organic metals. In addition to this particular complex, Buravov *et al.* have reported the isolation of a complex with $n\simeq 1$ and Kamaras *et al.* have found a complex with the composition range from $n=2.6$ to 2.9.[2,3] Moreover, the preparation of the complex TTT–$I_{0.72}$ has been described by Kathirgamanathan and Rosseinsky.[4] We examined earlier the electrical resistivity and thermoelectric power of TTT–I_n as functions of n using polycrystalline compactions.[5] Our resistivity-composition isotherm at 25 °C showed a minimum of 0.3 Ω cm at the composition of the metallic phase, TTT–$I_{1.5}$, and a shoulder as large as 200 Ω cm at the other phase, TTT–$I_{2.7}$. The presence of the latter phase was also manifested by a drastic increase in the thermoelectric power near $n=2.7$. No singularity due to the other complexes, TTT–$I_{0.72}$ and TTT–I, could be detected by these techniques, however.

The same techniques were employed for the elucidation of the TTT–Br_n complexes.[6] A minimum of about 7 Ω cm found near $n=0.5$ in the resistivity-composition isotherm at 25 °C indicated the formation of a mixed-valence complex, $(TTT)_2{}^+Br^-$. The resistivity increases monotonously up to $n=1.4$ and then abruptly by a factor of forty between $n=1.4$ and 1.5. This change implies the formation of another mixed-valence complex having the ideal composition of $(TTT)_2{}^{3+}(Br^-)_3$. The latter anomaly is accompanied by an increase of the activation energy for semiconduction by a factor of almost two and also by the change of sign in the variation of the thermoelectric power with the temperature from positive to negative. Here again, no indication of a well-established monobromide TTT^+Br^- was found by these techniques.

As our experiments on solid-state galvanic cells involving reactions between silver and the halogen in electronically-conducting thiazine–iodine complexes had provided a powerful tool for elucidating the constitution,[7] we decided to extend the work to the TTT–I_n and TTT–Br_n complexes. The electromotive force (emf) depends on n quite differently from the electrical resistivity and the thermoelectric power studied before. Two-phase mixtures should be identified by a constant emf, a stoichiometric complex by a discontinuous increase and a nonstoichiometric single-phase region by a continuous increase in emf with n.

Experimental

Materials. TTT was synthesized following the method reported by Marschalk and Stumm and recrystallized at least three times from 1,2,4-trichlorobenzene.[8] TTT–I_n samples were prepared by grinding the weighed TTT and iodine in an agate mortar in the presence of a small amount of benzene. The iodine contents were determined by elemental analysis. An additional sample prepared by the reaction between TTT and iodine in boiling nitrobenzene has a composition of $n=1.53$.

$TTT^{2+}(Br^-)_2$ was prepared by the oxidation of powdered TTT suspended in 1,2,4-trichlorobenzene with bromine, as described by Marschalk and Niederhauser.[9] The samples with n values less than two were obtained by grinding the weighed dibromide and TTT. The exact compositions were determined by microanalysis.

Measurements. The galvanic cell, Ag|AgI|TTT–I_n, was assembled. It was found to be necessary to mix intimately the electrolyte and TTT–I_n and to thermostat the cell at 80 °C for several days to attain an initial constant emf. The measurements were carried out in the range from room temperature to 80 °C, only for increasing temperatures. The cell was kept at each temperature for about one hour. The emf was read by means of a high-impedance universal digital meter, Yokogawa 2502. The work on the Ag|AgBr|TTT–Br_n cells was found to be more difficult. Reproducible emf values could be obtained only above 50 °C and only when the cell was kept for several days at each temperature.

Results and Discussion

TTT–I_n Complexes. The compositional variation of the emf at 25 °C is presented in Fig. 1. Below $n=1$, the cell maintains an emf of 491 mV. The samples in this composition range are supposed to be mixtures of the parent organic compound TTT and its iodine complex, TTT–I. The present work failed to provide any evidence supporting the existence of the TTT–$I_{0.72}$ reported by Kathirgamanathan and Rosseinsky. The emf increases continuously between $n=1$ and 1.5, suggesting the formation of a nonstoi-

Table 1. Thermodynamic data for the complex formation reaction, $\mathrm{TTT}+n/2\,\mathrm{I_2} \longrightarrow \mathrm{TTT\text{-}I}_n$

n	ΔG/kJ mol^{-1}	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	$(\Delta G/n)$/kJ mol^{-1}
1	−18.8	−21.1±1.1	−7.6±3.7	−18.8
1.5	−26.7	−27.7±1.3	−3.2±4.3	−17.8
2.7	−37.4	−35.8±2.5	5.3±5.2	−13.9
2.9	−38.8	−37.1±3.3	5.7±7.8	−13.6

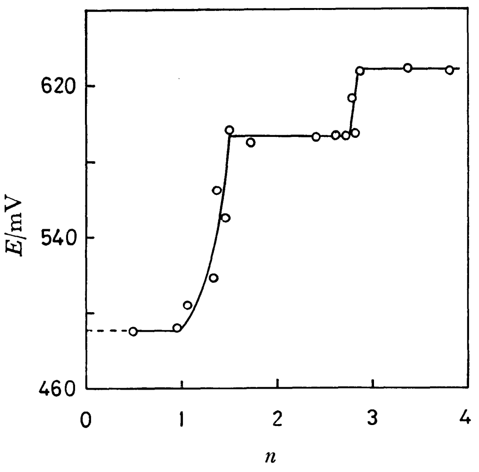

Fig. 1. Electromotive force of the solid-state cell, Ag|AgI|TTT–I_n *versus* n at 25 °C.

chiometric complex covering this range. In addition to the work by Buravov *et al.* mentioned above, Kamaras *et al.* have noted that TTT–I can be produced occasionally together with TTT and TTT–$\mathrm{I_{1.5}}$. The compositions of these two complexes are identified as the lower and upper limits of a nonstoichiometric phase. Kaminskii *et al.* have reported that the iodine content in the complex TTT–$\mathrm{I_{1.5}}$ may be varied from 1.5 to 1.55.[10] Apparently, the existence region of this nonstoichiometric phase is not limited to such a narrow range.

A plateau indicative of a two-phase region appears between $n=1.5$ and 2.7, giving an emf of 593 mV. The continuous increase observed between $n=2.7$ and 2.9 implies that the complex is again homogeneous over this range. In other words, a nonstoichiometric complex is formed. These results are in fair agreement with the observation made by Kamaras *et al.*, namely, the composition of recrystallized samples ranges from $n=2.6$ to 2.9 and the resistivity value along the needle axis is scattered by a factor of 16.[3] The occurrence of this phase was already confirmed by our resistivity and thermoelectric power measurements. The emf is 628 mV above $n=2.9$. The upper limit of this two-phase region could not be determined.

Since the current in AgI is exclusively carried by $\mathrm{Ag^+}$ ions, the emf values observed in the two-phase regions below $n=1$ and between $n=1.5$ and 2.7 yield the Gibbs energies of the following cell reactions:

$$\mathrm{Ag(s)} + \mathrm{TTT\text{-}I(s)} \longrightarrow \mathrm{AgI(s)} + \mathrm{TTT(s)} \quad \text{and}$$

$$\mathrm{Ag(s)} + 1/1.2\ \mathrm{TTT\text{-}I_{2.7}(s)} \rightarrow \mathrm{AgI(s)} + 1/1.2\ \mathrm{TTT\text{-}I_{1.5}(s)}.$$

Two more cell reactions covering the single phase regions are conceivable. It is convenient to consider the Gibbs energies in terms of the reactions:

$$\mathrm{Ag(s)} + \mathrm{TTT\text{-}I(s)} \longrightarrow \mathrm{AgI(s)} + \mathrm{TTT(s)} \qquad (1)$$

$$0.5\,\mathrm{Ag(s)} + \mathrm{TTT\text{-}I_{1.5}(s)} \longrightarrow 0.5\,\mathrm{AgI(s)} + \mathrm{TTT\text{-}I(s)} \qquad (2)$$

$$1.2\,\mathrm{Ag(s)} + \mathrm{TTT\text{-}I_{2.7}(s)} \longrightarrow 1.2\,\mathrm{AgI(s)} + \mathrm{TTT\text{-}I_{1.5}(s)} \qquad (3)$$

and

$$0.2\,\mathrm{Ag(s)} + \mathrm{TTT\text{-}I_{2.9}(s)} \longrightarrow 0.2\,\mathrm{AgI(s)} + \mathrm{TTT\text{-}I_{2.7}(s)}. \qquad (4)$$

The energies associated with the reactions (1) and (3) are easily calculated to be −47.4 and −68.7 kJ mol^{-1}. As is evident from Fig. 1, these values represent the area under the emf-composition relation between the upper and lower n values defined in each cell reaction. Therefore, the Gibbs energies associated with the reactions (2) and (4), in which the nonstoichiometric complexes participate, may be estimated by a graphic integration to be −25.2 and −11.7 kJ mol^{-1} respectively.

Combining with $\Delta G^\circ_f(\mathrm{AgI}) = -66.2$ kJ mol^{-1},[11] the Gibbs energies in terms of the following complex formation reactions:

$$\mathrm{TTT(s)} + 1/2\,\mathrm{I_2(s)} \longrightarrow \mathrm{TTT\text{-}I(s)}$$

$$\mathrm{TTT(s)} + 1.5/2\,\mathrm{I_2(s)} \longrightarrow \mathrm{TTT\text{-}I_{1.5}(s)}$$

$$\mathrm{TTT(s)} + 2.7/2\,\mathrm{I_2(s)} \longrightarrow \mathrm{TTT\text{-}I_{2.7}(s)}$$

$$\mathrm{TTT(s)} + 2.9/2\,\mathrm{I_2(s)} \longrightarrow \mathrm{TTT\text{-}I_{2.9}(s)}$$

are determined as presented in Table 1. The emf of the cell was a linear function of the temperature for all the samples studied. The entropy changes for the cell reactions (1)—(4) are estimated to be 18.5±2.4, 5.6±0.6, 6.8±0.4, and 14.5±1.1 J K^{-1} mol^{-1} on the basis of the temperature coefficients. The application of Gibbs-Helmholtz equation yields enthalpies of −42.0±0.7, −23.5±0.2, −66.7±0.1, and −7.4±0.3 kJ mol^{-1} for these cell reactions. With the aid of $\Delta S^\circ_f(\mathrm{AgI}) = 14.6$ J K^{-1} mol^{-1},[11] the entropy changes in terms of the complex formation reactions can be computed, and then with $\Delta H^\circ_f(\mathrm{AgI}) = -61.8$ kJ mol^{-1},[11] the enthalpy changes can be estimated. The results are summarized in Table 1. It may be noted that the entropy change is positive above $n=2.7$, while it is negative below this composition.

The Gibbs energy divided by the number of iodine atoms is in the range from −13.6 to −18.8 kJ mol^{-1}. These values show that the affinity of TTT for iodine is undoubtedly larger than that of the thiazines estimated earlier: *e.g.*, −6.9 kJ mol^{-1} at $n=2.8$ in the phenothiazine complex and −11.8 kJ mol^{-1} at $n=2.7$ in the benzo[*a*]phenothiazine complex. The diffusion of iodine in the present complexes appears to be appreciably hindered by strong binding to TTT. As the passage of current results in quick mass-transfer

Table 2. Thermodynamic data for the cell reaction, $\Delta n\,\mathrm{Ag} + \mathrm{TTT\text{-}Br}_n \longrightarrow \Delta n\,\mathrm{AgBr} + \mathrm{TTT\text{-}Br}_{n-\Delta n}$

n	Δn	E/mV	ΔG/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	ΔH/kJ mol^{-1}
0.5	0.5	281	−13.6	7.5±0.3	−11.4±0.1
0.8	0.3	*	−10.3	4.6±1.3	−8.9±0.4
0.98	0.18	429	−7.5	8.7±1.2	−4.9±0.4
1.04	0.06	*	−2.6	2.9±0.2	−1.9±0.06
1.2	0.16	480	−7.4	8.1±0.1	−5.0±0.03
1.48	0.28	528	−14.3	10.8±0.1	−11.1±0.03
1.54	0.06	*	−3.2	2.3±0.1	−2.5±0.03
1.96	0.42	572	−23.2	15.9±0.4	−18.5±0.1

* One-phase region.

Table 3. Thermodynamic data for the complex formation reaction, $\mathrm{TTT} + n/2\,\mathrm{Br}_2 \longrightarrow \mathrm{TTT\text{-}Br}_n$

n	ΔG/kJ mol^{-1}	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	$(\Delta G/n)$/kJ mol^{-1}
0.5	−34.9	−38.8±0.1	−13.4±0.3	−69.7
0.8	−53.6	−60.0±0.5	−21.4±1.6	−67.0
0.98	−63.6	−73.2±0.9	−32.3±2.8	−64.9
1.04	−66.8	−77.3±1.0	−35.9±3.0	−64.2
1.2	−74.9	−88.4±1.0	−45.8±3.1	−62.4
1.48	−87.7	−105.4±1.0	−59.9±3.3	−59.3
1.54	−90.3	−108.9±1.0	−62.9±3.4	−58.6
1.96	−107.8	−132.6±1.1	−83.7±3.8	−55.0

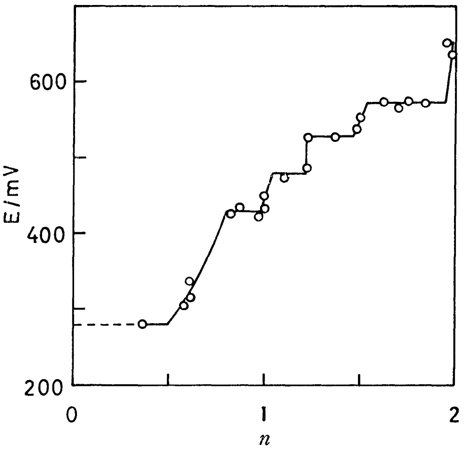

Fig. 2. Electromotive force of the solid-state cell, Ag|AgBr|TTT-Br_n *versus* n at 25 °C.

polarization, the application of a solid-state coulometric titration to the TTT-I_n complexes was found to be impracticable even if AgI is replaced with a highly-conducting AgI-based solid electrolyte.

We concluded that, on the basis of thermoelectric power, the TTT molecule in the iodine complex does not attain a unit positive charge even at $n=4.5$.[5] By contrast, both TTT^+ and TTT^{2+} bromides have been known by the work of Marschalk and Niederhauser.[9] The existence of these two has been fully supported by the significant differences in their electronic and vibrational spectra.[6,12] Consequently, one might foresee the appearance of many phases in the TTT-Br system in spite of the limitation of the study to the range $n<2$.

TTT-Br_n Complexes. In Fig. 2, the emf of the TTT-Br_n complexes extrapolated to 25 °C is plotted against n. When $n<0.5$, the cell exhibits an emf of 281 mV. An increase of the emf seems to be continuous between $n=0.5$ and 0.8. The lower limit coincides with the composition of the minimum resistivity found in the TTT-Br system. The emf remains at 429 mV until n reaches a little below one, and then increases continuously up to 480 mV in a relatively narrow range. Thus, the monobromide appears to be nonstoichiometric but only to the extent of 0.06. An abrupt increase in the emf at about $n=1.2$ from 480 to 528 mV suggests that this phase is stoichiometric or nearly so. The third single phase region appearing around $n=1.5$ corresponds to the mixed-valence compound $(TTT)_2{}^{3+}(Br^-)_3$ established by the resistivity-composition isotherm approach. The existence region is located from $n=1.48$ to 1.54; these values are a little higher than those reported before.[6] Then the two-phase region exhibiting an emf of 572 mV appears. Its upper limit is rather arbitrarily located at $n=1.96$.

The Gibbs energies, enthalpies, and entropies computed for the cell reactions, $\Delta n\,\mathrm{Ag(s)} + \mathrm{TTT\text{-}Br}_n\mathrm{(s)} \rightarrow \Delta n\,\mathrm{AgBr(s)} + \mathrm{TTT\text{-}Br}_{n-\Delta n}\mathrm{(s)}$, are summarized in Table 2. With the aid of $\Delta G_f^\circ(\mathrm{AgBr}) = -96.9$ kJ mol^{-1}, $\Delta H_f^\circ(\mathrm{AgBr}) = -100.4$ kJ mol^{-1}, and $\Delta S_f^\circ(\mathrm{AgBr}) = -11.7$ J K^{-1} mol^{-1},[11] the thermodynamic data for the complex formation reactions, $\mathrm{TTT(s)} + n/2\,\mathrm{Br_2(l)} \rightarrow \mathrm{TTT\text{-}Br}_n\mathrm{(s)}$ were estimated as given in Table 3. The Gibbs energy divided by the number of bromine atoms is in the range from −55.0 to −69.7 kJ mol^{-1}, indicating that bromine forms TTT complexes of greater stability than iodine does. The entropy changes are always negative. The order of magnitude is comparable with that known for the thiazine-iodine complexes. In conclusion, it must be emphasized that not only most of the complexes reported in earlier works but also some new phases have been established for both the iodine and bromine complexes by the present solid-state electrochemical study. The phases were found to be more or less nonstoichiometric.

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