Studies on the Photo-reproduction Type of Redox Cells.

I. Electrochemical Behavior of Aqueous Solutions of Methylene Blue / Ferrous Ion and Thionine / Ferrous Ion Systems under the Influence of Light

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An attempt was made to develop a new type of a device capable of converting the solar energy into electrical energy. It may be said that the new mode of device aimed here at belongs to a reproducible type of indirect fuel cells, in which photochemical reaction are to be utilized for the regeneration of the fuels consumed in the electrical discharging process. As for substances complying with the above requirements, some of the known organic substances, organic phosphorescent substances and organic redox dyestuffs should be considered. In the present study fundamental experiments were carried out in order to make clear the electrochemical behavior of methylene blue/ ferrous ion and thionine/ ferrous ion systems under irradiation by visible light. Somewhat detailed observations were made with a great emphasis on the effects of compositions, and particularly of the pH of the test solutions on the redox potentials. A remarkable result was that the presence of phosphate in the sample solutions played a decisive role in securing reproducible observations of potential-shifting phenomena caused by light.

1. Introduction

Being motivated by the rapid development of energy-conversion technology, attention has been lately called to the conversion of the solar energy into electrical energy. However, aside from the so-called "solar battery" which is actually based on the physical properties of semiconductors, no devices utilizing a chemical principle

have been developed yet. As a new method for realizing the energy conversion, it seems to be possible to construct a kind of a redox cell, in which both oxidants and reductants consumed in an electrical discharging process will be restored through photochemical reactions. From the technical point of view, it is apparent that methods and apparatus suitable for separating reductants from oxidants must be developed.

At this preliminary stage of this study, however, those important and interesting problems were laid aside. Instead, our interest was exclusively directed toward the electrochemical behavior of some kinds of substances conforming to the above mentioned purpose. As one of the substances complying with our requirement, a group of new phototropic substances derived of lophin, which had been found to exhibit a marked photochromism by Hayashi et al.¹⁾ has first called our attention.

With regard to these substances, however, we have not succeeded to establish the conditions necessary for observing reproducible redox potentials²⁾. The present paper includes only the results for the methylene blue/ferrous ion and thionine/ferrous ion systems, about which the conditions necessary for obtaining reproducible redox potentials have been established. It is well known that methylene blue together with thionine belong to a category of redox dyestuffs, physico-chemical properties of which have been most thoroughly examined³⁾.

Most of investigations concerned with these systems had been made on the photochemical aspect of the phenomena. However, a considerable number of problems belonging to the category of electrochemistry still remains unsolved. In the present study, the electrochemical behavior of aqueous solutions of both methylene blue/ferrous ion and thionine/ferrous ion systems were examined especially on the effects of the compositions of the solutions, together with the effect of the pH of them.

2. Experimental

Apparatus and Procedure

The whole layout used for measuring redox potentials under irradiation by visible light is shown in Fig. 1. The reaction vessel was a wide test-tube (*ca.* 4.3 cm in diameter, 15 cm long) equipped with a ther-

A: reactor vessel,
B: lamp
C: water container.

Fig. 1 Schematic drawing of the layout for measuring redox potentials under irradiation by visible light.

mometer and two electrodes; a saturated calomel electrode as a reference electrode and a platinum electrode for measuring redox potentials. Moreover, a long spiral glass tube for cooling was furnished to this vessel. Cooling of this vessel was effected by letting city water to flow through this tube so as to keep the temperature of the solution constant within $\pm ca. 0.1^\circ\text{C}$.

Potential differences between the above two electrodes were measured by the use of a pH meter (TOA Electronics Ltd., HM-5A type), the output current of which was fed to a pen recorder (ditto, EPR-2T type) through an amplifier (ditto, Prebox). A tungsten lamp (Fuji projection lamp, 100 V, 150 W. or Elmo projection lamp, 21.5 V, 150 W.) was used as a source of visible light. During the irradiation, the position of the light source was fixed at 10 cm from the reactor vessel. A water-filled vessel was placed between the light source and the reactor vessel, in order to minimize the intensity of thermal rays reaching the latter.

A known amount of test solution (100 cc) of the required composition was put into the

reaction vessel. Irradiation and its subsequent interruption were repeated alternately at 15-minute intervals. Temporal variation of redox potentials accompanying this procedures were followed by the pen recorder mentioned above. Moreover, a rotating sector method was adopted to get a better insight into the mechanism of the investigated reaction. Four kinds of sectors were employed, each of which had a different number of sections. This sector driven by a synchronous motor (Oriental Motor Co. Ltd., 4SQ10, 1500 r.p.m.) fitted with a gear head (ditto, 4G5, deceleration ratio 1 : 5) was placed between the reactor vessel and the light source.

- A: platinum-net electrode
- B: platinum-plate electrode
- C: saturated calomel electrode
- D: lamp
- E: glass tubing for cooling water

Fig. 2 Top view of the photochemical cell for making a preliminary test.

A few experiments were conducted using a photochemical cell, in which the system described above was employed as a mediating substance. As shown in Fig. 2 the photochemical cell, made of a transparent resin plate, was designed to have two chambers separated by a thin plate so as to prevent photo-products from mixing with original reactants. One chamber irradiated by light from its side face was provided with a platinum-net electrode, a thin glass-

tube for cooling and the rotor of a magnetic stirrer. Cooling was again effected by flowing city water. Another chamber covered by black paper was provided with a platinum-plate electrode. Since the plate separating the two chambers had a lot of small holes in order for solute ions to pass through them, electric current could pass through it owing to the migration or diffusion of ions. Under the irradiated conditions the platinum-net electrode of the former chamber became surrounded by a completely decolorized solution only. Accordingly, there seems to be no local polarization on the electrode surface.

Test Solutions

Test solutions of the methylene blue/ferrous ion system were obtained by mixing four "stock solutions", prepared beforehand, in the required proportions. These four liquids were $4.5 \times 10^{-5} M$ methylene blue aqueous solution (A-liquid), $0.5 M$ ferrous sulfate with sulfuric-acid acidity (B-liquid), $0.5 M$ sodium dihydrogen phosphate solution (C-liquid) and pure water (D-liquid). Compositions of solutions thus prepared are shown in Table 1 where a part of the experimental data was also listed. With respect to the thionine/ferrous ion system, solutions of similar compositions were prepared as shown in Table 2. A series of experiments were conducted only about the system of methylene blue. The concentration of phosphate was changed together with a stepwise variation of the concentration of acetic acid as shown in Table 3. Since the total volume of the test solutions used in each run was always 100 cc for Run I through Run IV, both the content of methylene blue and that of ferrous sulfate were retained constant.

3. Results

Effects of Ferrous Sulfate Concentration

Aqueous solutions containing methylene

Table 1 Redox Potentials of Methylene Blue/Ferrous Ion System When the Content of Na_2HPO_4 was Changed (at 10°C)

Number of run	Composition of solution				pH	Redox potentials* under darkness condition mV	Redox potentials under light condition mV	Shifts of potentials** due to irradiation mV
	A-liquid cc	B-liquid cc	C-liquid cc	water cc				
1	40	2	0	58	1.58	289	289	0
2	"	"	1	57	1.59	251	211	40
3	"	"	2	56	1.62	240	139	101
4	"	"	3	55	1.68	232	130	102
5	"	"	5	53	1.78	222	116	106
6	"	"	10	48	1.92	208	99	109
7	"	"	20	38	2.20	177	77	100
8	"	"	30	28	2.38	147	61	86
9	"	"	45	13	2.53	120	52	68
10	"	"	58	0	2.67	100	42	58

* Redox potentials were measured with reference to a saturated calomel electrode.

** Shifts of potentials were expressed in terms of absolute values.

Table 2 Redox Potentials of Thionine/Ferrous Ion System When the Content of Na_2HPO_4 was Changed (at 10°C)

Number of run	Composition of solution				pH	Redox potentials under darkness condition mV	Redox potentials under light condition mV	Shift of potentials due to irradiation mV
	A-liquid cc	B-liquid cc	C-liquid cc	water cc				
1	40	1	0	59	1.82	299	—	0
2	"	"	1	58	1.88	289	181	108
3	"	"	2	57	1.93	270	159	111
4	"	"	3	56	2.00	262	152	110
5	"	"	5	54	2.12	247	142	105
6	"	"	10	49	2.37	212	130	82
7	"	"	20	39	2.62	172	115	57
8	"	"	40	19	3.05	130	94	36

Table 3 Compositions of Sample Solutions of Methylene Blue/Ferrous Ion System When Contents of Both Phosphate and Acetic Acid were Changed (40 cc of A-liquid and 2 cc of B-liquid were taken in each run)

Series	Number of run	C-liquid cc	Acetic acid cc	Water cc	pH	Shifts of redox rotentials (mV)
I	1	0	0	58	1.58	0
	2	1	"	57	1.59	40
	3	2	"	56	1.62	101
	4	3	"	55	1.68	102
	5	5	"	53	1.78	106
	6	10	"	48	1.92	109
	7	20	"	38	2.20	100
	8	30	"	28	2.38	86
	9	45	"	13	2.53	68
	10	58	"	0	2.67	58
II	1	0	1	57	1.57	3
	2	1	"	56	1.60	52
	3	2	"	55	1.65	97
	4	3	"	54	1.70	100
	5	5	"	52	1.79	104
	6	10	"	47	1.98	109
	7	20	"	37	2.22	102
	8	30	"	27	2.38	85
	9	45	"	12	2.48	67
	10	57	"	0	2.52	55
III	1	0	3	55	1.67	0
	2	1	"	54	1.67	47
	3	2	"	53	1.72	93
	4	3	"	52	1.72	95
	5	5	"	50	1.84	99
	6	10	"	45	1.97	104
	7	20	"	35	2.18	99
	8	30	"	25	2.29	84
	9	45	"	10	2.39	62
	10	55	"	0	2.47	52
IV	1	0	5	53	1.68	3
	2	1	"	52	1.68	37
	3	2	"	51	1.69	90
	4	3	"	50	1.73	93
	5	5	"	48	1.82	94
	6	10	"	43	1.88	100
	7	20	"	33	2.16	94
	8	30	"	23	2.28	81
	9	40	"	13	2.30	66
	10	53	"	0	2.40	56

Fig. 3 a) Plots of redox potential against concentrations of FeSO₄ (methylene blue).

Fig. 3 b) Plots of redox potentials against concentrations of FeSO₄ (thionine).

blue or thionine alone have redox potentials of ca. 80 mV with reference to a saturated calomel electrode. The redox-potential of this solution did not undergo any appreciable effect by the irradiation of light.

As shown in Fig. 3 (with respect to thionine), the redox potentials of this solution under darkness increased with the increasing concentration of ferrous sulfate and then reached a certain fixed value which was governed essentially by the ferric/ferrous ion system. When concentration of ferrous sulfate was made slightly higher, effects of light became appreciable, and furthermore the reproducibility of the potential-shift phenomena, though incomplete, was made slightly better.

Effects of Phosphate Potential

Measurements

As shown in Fig. 4 a) and b), when phosphate was not present at all, no reproducible behavior of the redox potential was observed under irradiation by light.

Fig. 4 a) Redox potential of methylene blue when phosphate was not included.

On the contrary, when phosphate was present in the solution, reproducibility was fairly good for both the methylene

Fig. 4 b) Redox potential of thionine when phosphate was not included.

blue/ ferrous ion and thionine/ ferrous ion systems, as shown in Fig. 5 a) and b). Borate was also found to exhibit a similar effect, though it was not so marked as in the case of the phosphate.

Fig. 5 a) Redox potential of methylene blue when phosphate was included.

Fig. 5 b) Redox potential of thionine when phosphate was included.

Dependence of Redox Potentials on pH

Redox potentials under the steady-state conditions before and after the light was switched on were found to exhibit an approximately linear dependence on

Fig. 6 Dependence of redox potentials of thionine upon pH.

the pH of the solutions. As shown in Fig. 6, a relatively good linearity was obtained only in the case of thionine, while the linearity was not so good in the case of methylene blue.

Transitional Behavior of Redox Potentials Immediately after the Irradiation was Stopped

Upon closely examining the features of the curves recorded on a paper, two main modes of potential-changes could be distinguished depending on the values of the pH (cf. Fig. 7). For low values of pH the redox potential seemed to decrease in two steps, while for a slightly higher values of pH this potential was shown to decrease monotonously with time. It is interesting to note that the critical value of pH discerning these two kinds of behavior is ca. 2.22.

Fig. 7 Transitional behavior of redox potentials of methylene blue immediately after irradiation was switched off.

Dependence of Potential Shifts Induced by the Light Irradiation upon pH

Concerning the methylene blue/ferrous ion system, the dependence of potential shifts due to the irradiation on pH was

studied at different concentrations of acetic acid. Results are shown in Fig. 8. Potential shifts have maximum values near pH 1.9 irrespective of the concentration of acetic acid. Quite a similar tendency was observed with the thionine/ferrous ion system (cf. Fig. 9).

Fig. 8 Dependence of potential shifts due to the irradiation upon pH (methylene blue).

Fig. 9 Dependence of potential shifts due to irradiation upon pH (thionine).

Data Resulting from the Sector Method

The sector method commonly used in photochemistry was applied to the present system for the purpose of separating dark reactions involving electrode reactions from purely photochemical processes. Angles of the opened portion of the rotating discs were changed from 5° through 180° at interval of 5° , while the rotating speed was fixed to only 5 rev./sec. In this connection, four kinds of discs having different numbers of cut-out sections were designed in manner the depicted in Fig. 10. In Fig. 10, redox potentials, which have reached steady states values during the course of intermittent irradiation are plotted against the total angles of opened portions.

Total angle of opened sections (θ°) and ratio of opened sections to the entire area.

Fig. 10 Redox potentials in steady states when both angles of opened sections and number of divided sections of rotating discs are changed.

An Experiment Conducted by the Use of the Photochemical Cell

When a microammeter (100 μ A, 4.35 $k\Omega$ internal resistance) was inserted be-

tween the two electrodes, an output current of the photochemical cell of Fig. 2 was seen to reach ca. 22.0 μ A during the course of irradiation, when a mixed solution, for example, of A-liquid (400 cc), B(30 cc), C(50 cc) and D(20 cc) was used. Being measured with reference to the saturated calomel electrode, the redox potentials of the platinum-net electrode in the lighted chamber was found to exhibit the same kind of characteristics as shown in Fig. 5. It must be emphasized that such reproducible potential-shift phenomena as just mentioned can occur even in the case where the two electrodes of this cell are laid in a closed-circuit state, though the output power remains to be of a very minute value (2.1 μ W.).

4. Discussion and Conclusions

Though our study is still in a preliminary stage, several points of significance have come to light during the course of the study. One of our most remarkable findings was that the phosphate is effective in obtaining reproducible redox potentials under the irradiation. In this connection, attention must be paid to the fact reported by Koizumi et al.⁴⁾ In their report where the photo-reduction of methylene blue dissolved in water is dealt with under conditions free of reducing agent, it has been stated that the presence of phosphate or borate is imperatively necessary in order that reduction proceeds favorably. The fact that photo-reduction may occur in spite of the absence of any reducing agent becomes understandable when considering the possibility that the dyestuffs themselves may act as a reducing agent. In their report it has been also mentioned that the initial state of methylene blue solution before the photoreduction can be recover-

ed by aeration. In an ethanol solution of the same compound, photo-reduction of methylene blue is also accomplished, but the restoration of the initial state is incomplete. Presumably, excited species produced by chemical reactions might extract hydrogen atoms from methanol molecules to form side products which can no more return to the original substance. In the present case where the reducing agent (ferrous ion) coexists from the beginning, the function of phosphate seems to be different from that reported by the above investigators, though the existence of phosphate is of considerable importance in both cases.

As stated in the previous section, in the region below pH 2.22, the characteristic decrease in the redox potential were found to be composed of two steps. Since it has been assumed so far that a semiquinone-type intermediate does play an important role in the mechanism of the reaction under discussion, the aforementioned singular feature of the temporal change of the redox potential might be related to this semiquinone. However, it is open to contention whether such a temporal change associated with the electrode reaction, i.e., a kind of surface reaction, will coincide with the velocities of reverse reaction occurring in the bulk of the solution.

In the preceeding section, our efforts were exclusively concentrated to describe experimental results as precisely as possible, purposely refraining from theoretical consideration. This is essentially because evidences obtained as yet are insufficient to enable a complete understanding of the details of the reaction. At any rate, much work remains to be done before any conclusion can be drawn concerning some important factors, such as the quantum yield of the dark reaction, a kind of half life of the reduced state,

the efficiency of energy transfer in each elementary process involved, and so on.

For the purpose of preparing the photo-reproduction type of redox cells, the following technical problems must be investigated. In the first place a technical method must be known for separating reductants from oxidants, both of which are produced by the photo-chemical reaction. Second, the whole layout capable of passing photo-products through the redox cell, the reactor vessel in which the photochemical reaction takes place, and the apparatus for the separation of reductants from oxidants, all in one succession, has still to be designed.

Further details obtained by means of the sector method, which is now being continued, will be reported in a later paper.

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