3. EXPERIMENTAL

A. Materials

1. ferrous sulfate heptahydrate (BDH)
2. ferric sulfate (Fluka)
3. disodium salt of ethylenodiaminetetraacetic acid (E. Merk)
4. hydroquinone (E. Merk)
5. hydrazinium dichloride (E. Merk)
6. hydroxylamine, hydrochloride (Fluka)
7. hydrazinium sulfate (E. Merk)
8. diethanolamine (E. Merk)
9. triethanolamine (E. Merk)

   These reagents were analytical grade.

10. organic dyes:
    - thionine (Lauthshes Violett, Fluka)
    - methylene blue (E. Merk)
    - gallocyanine chloride (E. Merk)
    - nile blue (BDH)
    - tolusafranine (fluka)
    - neutral red (Dain Brothers, LTD.)
    - crystal violet (E. Merk)
    - acridine orange (BDH)
    - flourescein (E. Merk)
    - methyl violet 6B (E. Merk)
    - eosin gelblich (E. Merk)
    - riboflavin (E Merk)
    - indigo carmine, aqueous solution (The Government Pharmaceutical Organization)

- variamine blue (E. Merk)

etc.

All chemicals were used without further purification.

B. Apparatus

A medium pressure mercury lamp (Philips 93136 E, 0.9 A.) was used as the light source for photogalvanic study. The light intensity at the cell position was about 6.7 mW cm^{-2} (measured by Pyranometer AR-2000 RS, Yokoyama Ehectric Works., Ltd.). For preliminary work, the photoelectrochemical measurements were performed in a glass cell shown in Figure 8. The cell consists of two chambers, light and dark, separated by a light-intercepting black plate. This plate protects one chamber from the light but allows a free flow of the solution which was circulated by means of a magnetic stirrer during the reaction period. The cell was equipped with a calomel electrode (1N. KCl solution) in the dark chamber and a bright 0.8-cm^2 platinum plate electrode in the illuminated chamber for photopotential measurements. For photocurrent measurements, two 0.8-cm^2 platinum electrodes were used in both chambers. The illuminated electrode was placed in such a way that it was parallel to the incident light to minimize direct photoelectric effect (Becquerel effect). The distance between two electrodes was about 2 cm.

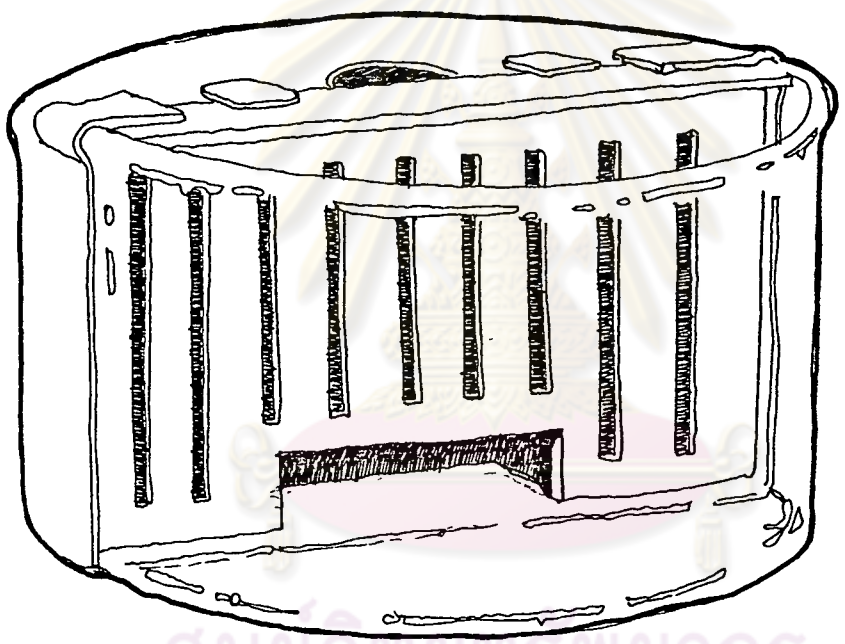

Figure 8. Cell for preliminary investigation of photogalvanic effects.

The second cell used in the experiment was a Pyrex glass cell shown in Figure 9. The cell consists of light and dark compartments connected by an arm which allows a free flow of solution. Circulation of the solution in both compartments was achieved by bubbling with nitrogen gas. The flow rate of the gas was kept constant at approximately 20 l min^{-1}. The two compartments were provided with separate Pyrex jackets through which water of requisite temperature was circulated from a temperature-controlled water bath. The electrodes were placed in the same manner as described earlier but their separation was now 8.5 cm. This type of cell was used to study the effects of various variables on the photogalvanic systems.

For potential measurements, a KEITHLEY 130 digital multimeter was used and for current measurements, a Goerz Electro UNIGOR 6e (type 226236) multimeter was used. A SCHOTT GERÄTE CG 811 pH-meter was used for pH measurements.

UV-VIS spectra of the organic dyes and all reacting solutions were recorded at room temperature ($\sim 29^{o}C$) on a Shimadzu UV-VIS spectrophotometer (Model UV-240).

The ultraviolet spectrum of the Pyrex cell used in this experiment was recorded on a Jasco HMC 358 UVIDEC-650 Double Beam Spectrophotometer at room temperature.

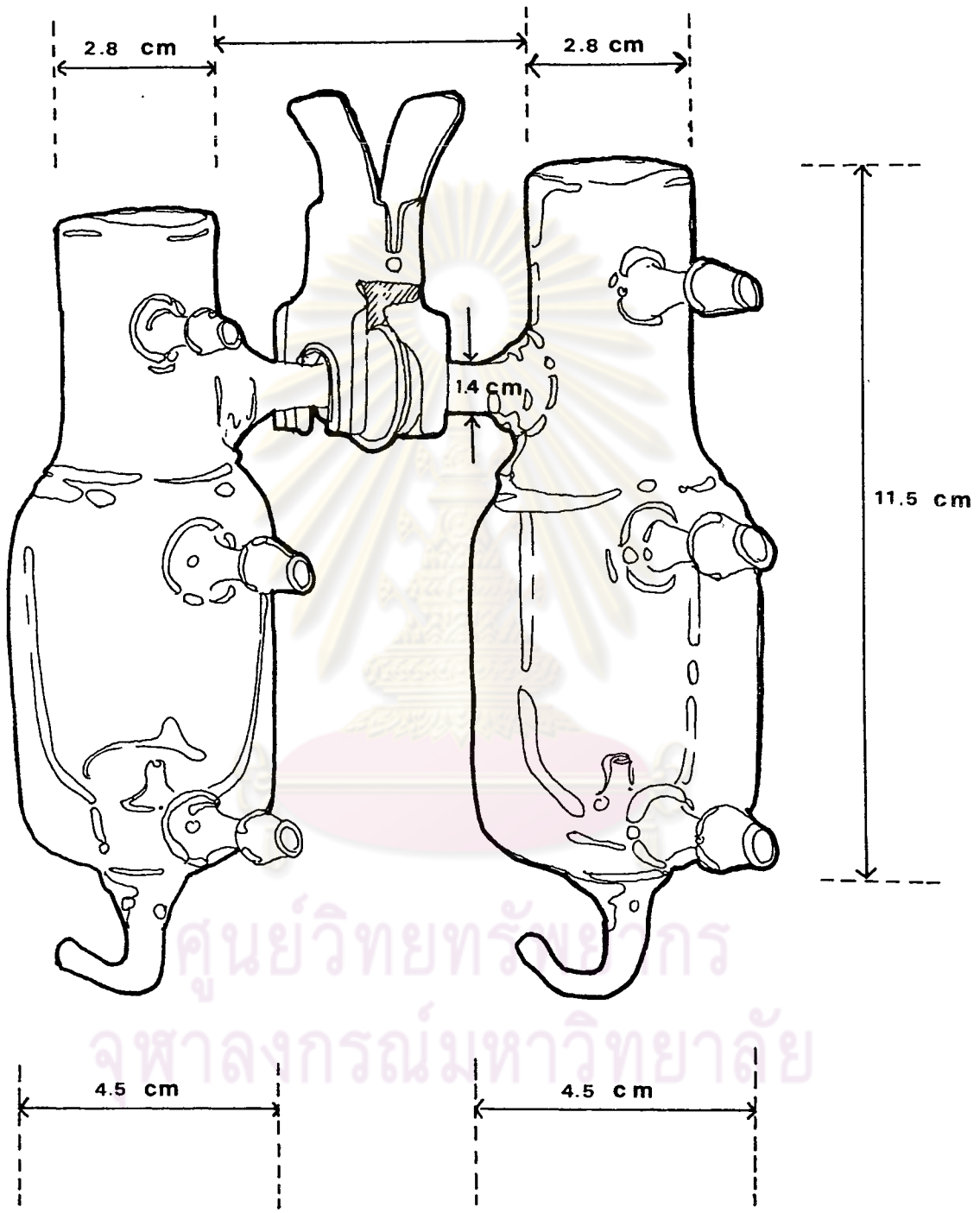

Figure 9. The second type of cell for detailed investigation of photogalvanic effects.

C. Methods

1. Selection of suitable photogalvanic systems

Each organic dye-redox pair system (e.g. thionine-diethanolamine, methylene blue-triethanolamine, or crystal violet-EDTA,...., etc.) was illuminated by the same light source in order to test the ability to exhibit photogalvanic effects.

A total of 120 aqueous systems were tested using the preliminary cell (Figure 8.) placed 6.5 cm away from the light source. Each system contained 200 cm^3 of 0.05 mol dm^{-3} solution of the non-light absorbing redox couple (except for iron (II) sulfate and EDTA whose concentrations were 0.01 and 0.10 mol dm^{-3}, respectively) and a few drops of the aqueous dye solution. The mixture was continuously stirred and the potentials were measured before and during illumination. Potentials of the systems which exhibit photogalvanic effects will change (increase or decrease) within a few minutes after the solutions have been illuminated. Systems with the highest photopotentials were selected for further study.

2. Photopotential measurements

The Pyrex glass cell (Figure 9.) was used to investigate the photopotential properties. It was equipped with 1N calomel electrode in the dark compartment and platinum electrode in the illuminated compartment. Both electrodes were connected to the multimeter.

The distance between electrodes was constant at 8.5 cm and that between the light source and cell surface was 8 cm. The total volume of redox solution was 80 cm^3 and that of the dye was 1.0 cm^3. The potential was first measured in the dark and the potential change over illumination period were recorded until an equilibrium value was reached.

2.1 Effect of concentration

For each photogalvanic system obtained from 1, the concentration of non-light absorbing compound was varied (the total volume was always 80 cm^3) while the concentration of the dye was kept constant. The variation of photopotential with concentration was recorded. Similarly, the concentration of the dye was varied while that of non-absorbing material was kept constant. The optimum concentrations for each system at room temperature ($\sim$ 29 ^{o}C) were then determined.

2.2 Effect of pH

The pH of the photogalvanic solution from 2.1 was adjusted by adding 1 mol dm^{-3} HCl or 5 mol dm^{-3} NaOH aqueous solution before illumination. The photopo-tential at each pH was measured at room temperature. The pH variation was between 2 and 12.

2.3 Effect of temperature

The photogalvanic system with optimum conditions of concentrations and pH was placed in the

cell around which water of requisite temperature was circulated. While the temperature of illuminated compartment was varied, the dark compartment temperature was maintained constant at 29 °C and vice versa. Finally, the temperature of both compartments was varied simultaneously to observe the difference of this effect on the photopotential. The temperature variation was between 29 °C and 80 °C.

2.4 Effect of oxygen gas

All procedures were the same as those described before but oxygen gas with a constant flow rate ($\sim$ 15 l min^{-1}) was bubbled through the photogalvanic solution during and after illumination.

2.5 Effect of organic solvents

The following organic solvents, which are miscible with water, were chosen:

1. CH_3OH
2. C_2H_5OH
3. $CH_3CHOHCH_3$
4. $(CH_3)_3COH$

1.0 cm of the organic solvent was dropped into the aqueous photogalvanic solution (optimum conditions, at room temperature) either in the dark or after the maximum photopotential had been obtained during illumination.

3. Photocurrent measurements

A bright 0.8-cm^2 platinum plate electrode was located at each half cell compartment in such a way that it is parallel to the incident light.

3.1 Effect of temperature

The variation of photocurrent with the temperature of the illuminated compartment, the temperature of the dark compartment and that of both compartments was studied in an identical way to the variation of photopotential with temperature (2.3). The electrodes were 8.5 cm apart. (Figure 10).

3.2 Effect of oxygen gas

Oxygen gas was bubbled through each compartment alternately and then through both compartments while measuring the photocurrent. The electrodes were 8.5 cm apart.

3.3 Effect of diffusion length

The diffusion length of the photoreacting species between the two compartments was varied by moving both electrodes up or down as illustrated in Figure 11.

The diffusion length was taken as the average distance that active species moved from one electrode to the other. For example, with the electrodes in position (b) in Figure 11, the diffusion length was 0.6 + 2.6 + 8.2 + 2.6 + 0.6 = 14.6 cm. In this experiment, the diffusion length was varied from 9.0 cm to 25.0 cm, and its effects on the maximum photocurrent (PC_{max}) and equilibrium value (PC_{eq}) were recorded.

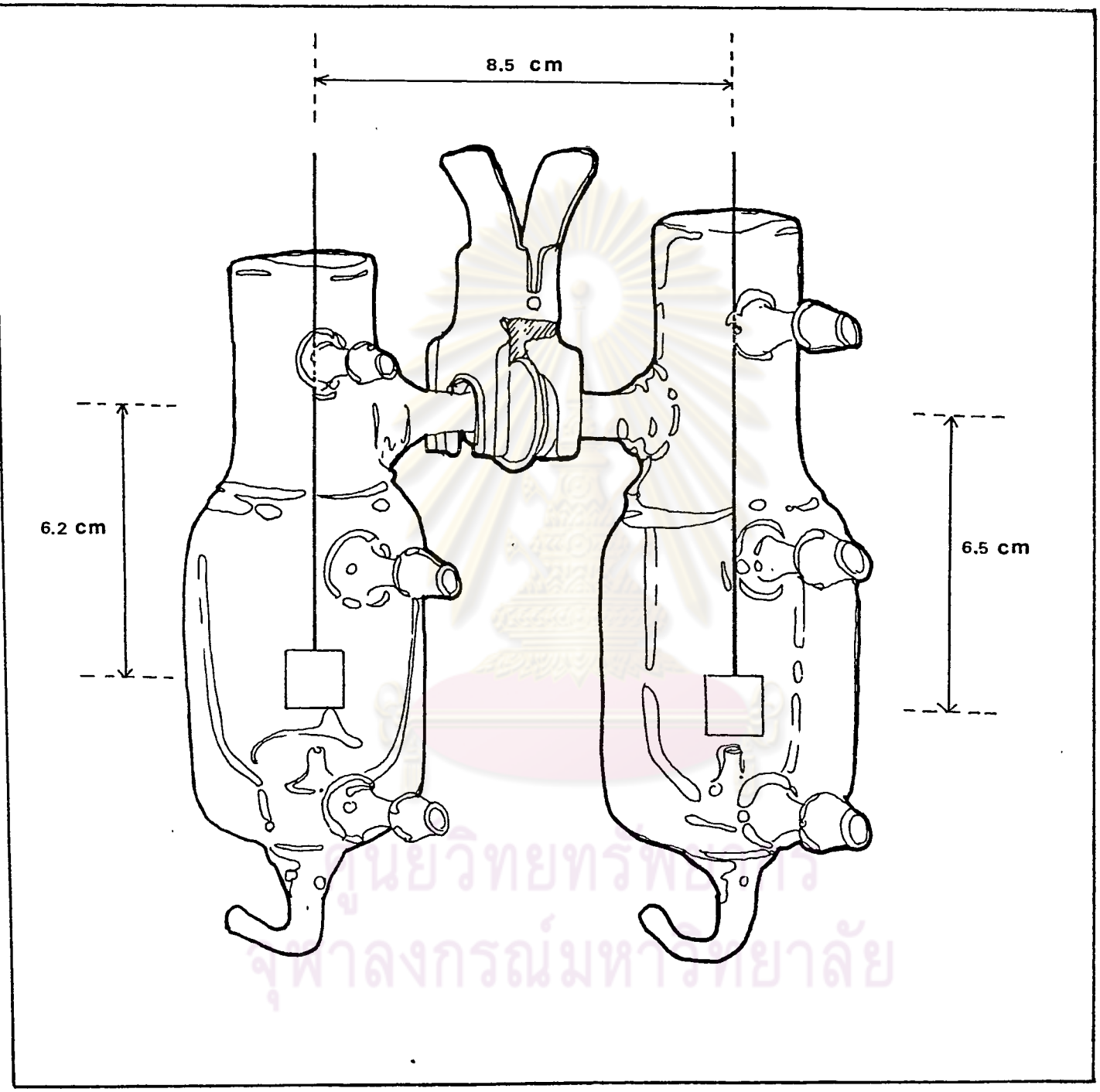

Figure 10. The positions of platinum electrodes for investigation of the temperature and oxygen gas effects on photocurrent.

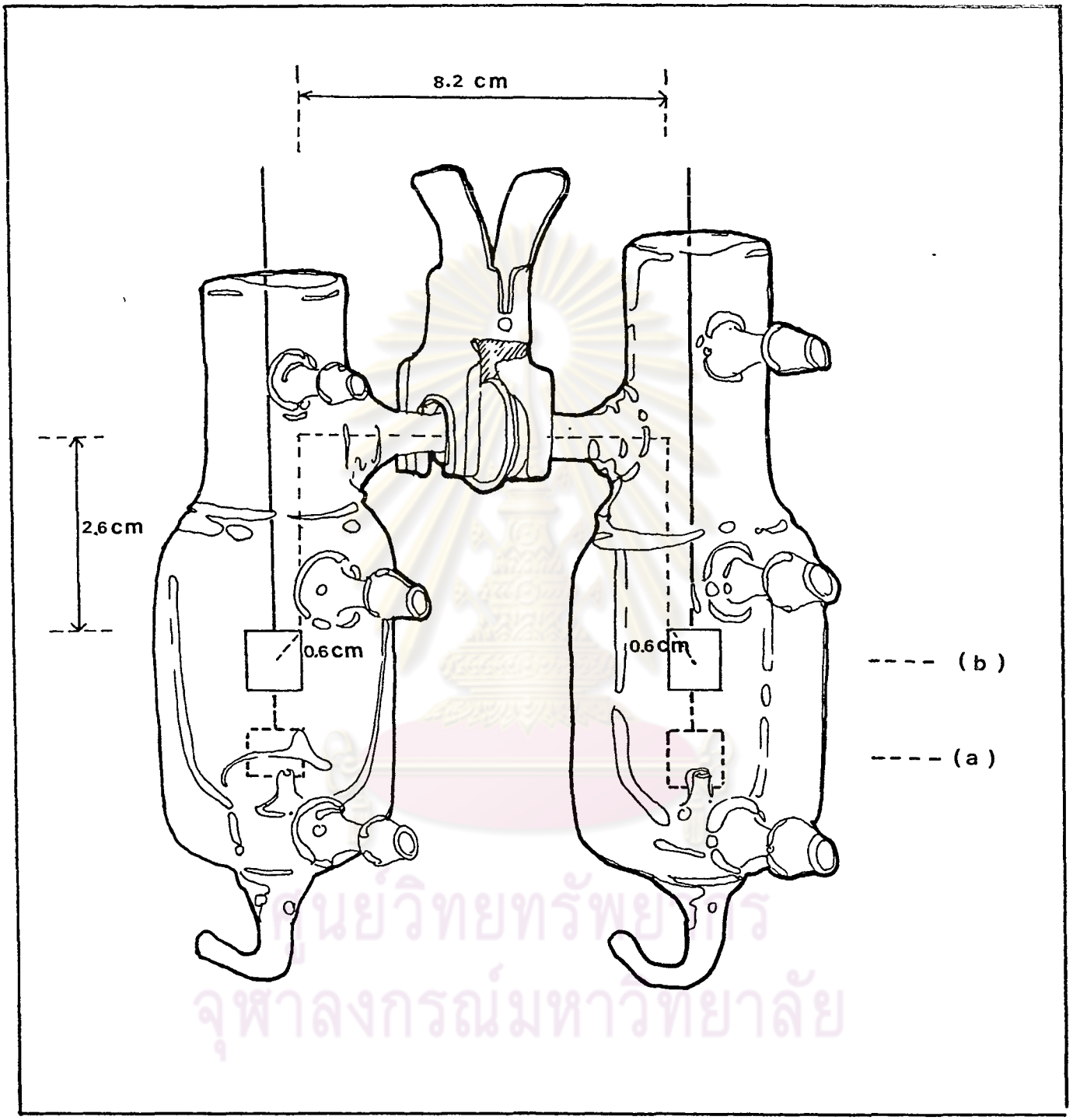

Figure 11. The variation of diffusion length between the electrodes.