

4. RESULTS AND DISCUSSION

4.1 Selection of the appropriate photogalvanic system

In principle, any system containing two redox couples, one of which is photoactive, can exhibit the photogalvanic effect. However, this may or may not be experimentally detectable. The maximum photopotential obtainable from a photogalvanic system depends primarily on the relative positions of equilibrium of the system in light and in the dark. It is extremely difficult to predict the ability of any system to exhibit a detectable photogalvanic effect because of the following reasons:

(i) The exact identities of the species involved in each redox reaction are usually unknown. Data on reduction potentials are thus available only for a few dyes, e.g. thionine and methylene blue.

(ii) The primary step of photochemical redox reactions is usually a single electron-transfer reaction. The excited dye molecule may either receive or lose one electron. Nevertheless, the available redox potential data (34-36) for most organic dyes correspond to two-electron transfer reactions. This means that they all undergo two electron reductions electrochemically.

(iii) The relevant values of the redox potential must be those of organic dyes in their excited state. It is difficult and complicated to define and obtain the redox potential of excited species although the redox

behavior of dyes in the excited state is governed almost exclusively by the ground state redox potentials and the excitation energy (36). Therefore, there is no direct relationship between the redox potential of an organic dye and that of the non-light absorbing redox couple for the prediction of photogalvanic behavior.

(iv) Knowledge of redox potentials does not necessarily mean that such a prediction can be made. The sensitivity of the system, however, may be related to the potential difference of the redox couples (5b).

(v) The photoinduced potential which is the primary sign of photogalvanic response, is most likely to be determined by the type of active (electron donating or electron accepting) species near both electrodes. If detailed information on the reaction mechanism is not known, no prediction can be made.

In this experiment the photogalvanic systems were obtained by testing for the photogalvanic effect in a total of 120 systems. This was done by plotting the potential response (to illumination) of each cell versus time. The photoinduced potential (or photopotential) is taken as the difference between the dark potential and the potential in the photostationary state. Results are shown in Table 3.

From Table 3 it can be seen that only two systems (riboflavin-diethanolamine and riboflavin-triethano-

Table 3. Photoinduced potential (mV) of tested 120 systems.^a

Organic dye non-light absorbing redox couple	thionine 10 ⁻⁴ M.	methylene blue 10 ⁻⁴ M.	galloxyanine chloride, 10 ⁻⁴ M.	nile blue 10 ⁻⁵ M.	safranin T 10 ⁻⁴ M.	neutral red	crystal violet 10 ⁻⁵ M.	acridine orange	fluorescein	methyl violet 6B	rhodamine B	eosin gelblich	riboflavin 10 ⁻⁴ M.	indigo carmine	variamine blue
ferrous sulfate in 0.05 M.H ₂ SO ₄ (1) ^b	67	36	-	54	-	51	-	-	83	-	-	-	-	-	2
EDTA (5)	173	148	95	-	602	-	30	-	-	-	-	-	557	-	50
hydroquinone (8)	-	-	-	8	-	17	13	23	-	18	5	2	-	-	-
hydrazine sulfate (1)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
hydroxylamine hydrochloride (2)	-	26	-	10	-	-	-	-	-	-	-	-	-	-	-
hydrazinium dichloride (1)	16	-	-	-	-	-	-	-	-	-	-	-	-	-	-
diethanolamine (10)	68	111	64	55	52	146	-	-	-	31	-	151	325*	-	-
triethanolamine (9)	152	214	-	-	46	-	-	29	248	97	-	205	364*	53	-

a : all conditions and instrument are described in the experimental section (1)

b : approximate pH in aqueous solution

- : no photogalvanic effect

* : selected photogalvanic system

amine) show photopotential responses in excess of 300 mV. (In the ferrous iron-thionine system the photopotential is only 250 mV). These systems are thus selected for further studies.

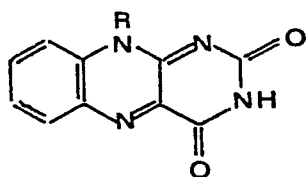
4.2 The Riboflavin (Rb)-Diethanolamine (Dea) System

4.2.1 Photopotential study

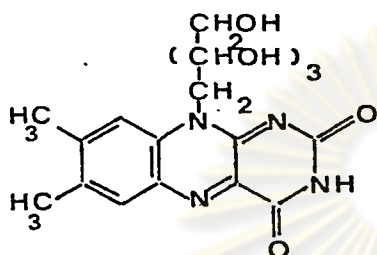
Riboflavin (6,7-dimethyl-9-[1-D-ribityl] isoalloxazine ; vitamin B₂ ; lactoflavin) is a yellow-colored dye in the isoalloxazine group. Its structure is shown in Figure 12. Riboflavin has absorption maxima at 337 and 445 nm at pH 7.4 (Figure 13).

Diethanolamine ((OHCH₂CH₂)₂NH) has no absorption in the visible but absorbs in the ultraviolet region. The spectrum is shown in Figure 14. It was found that the double-walled Pyrex cell (Glass no. 5510) used in this experiment absorbs most of the ultraviolet radiation from the light source. Its absorption spectrum is shown in Figure 15. It can, therefore, be assumed that only the visible portion of light from the light source was responsible for all photochemical reactions occurring in the systems under study.

The potential responses of the system to illumination cycles at the optimum condition, 2.5×10^{-2} mol dm⁻³ Dea, 1.2×10^{-4} mol dm⁻³ Rb at pH 8.43, is shown in Figure 16. The potential of the system in the dark was approximately 70 mV. Upon illumination the



(a)



(b)

Figure 12. The structure of (a) isoalloxazine compound; (b) riboflavin.

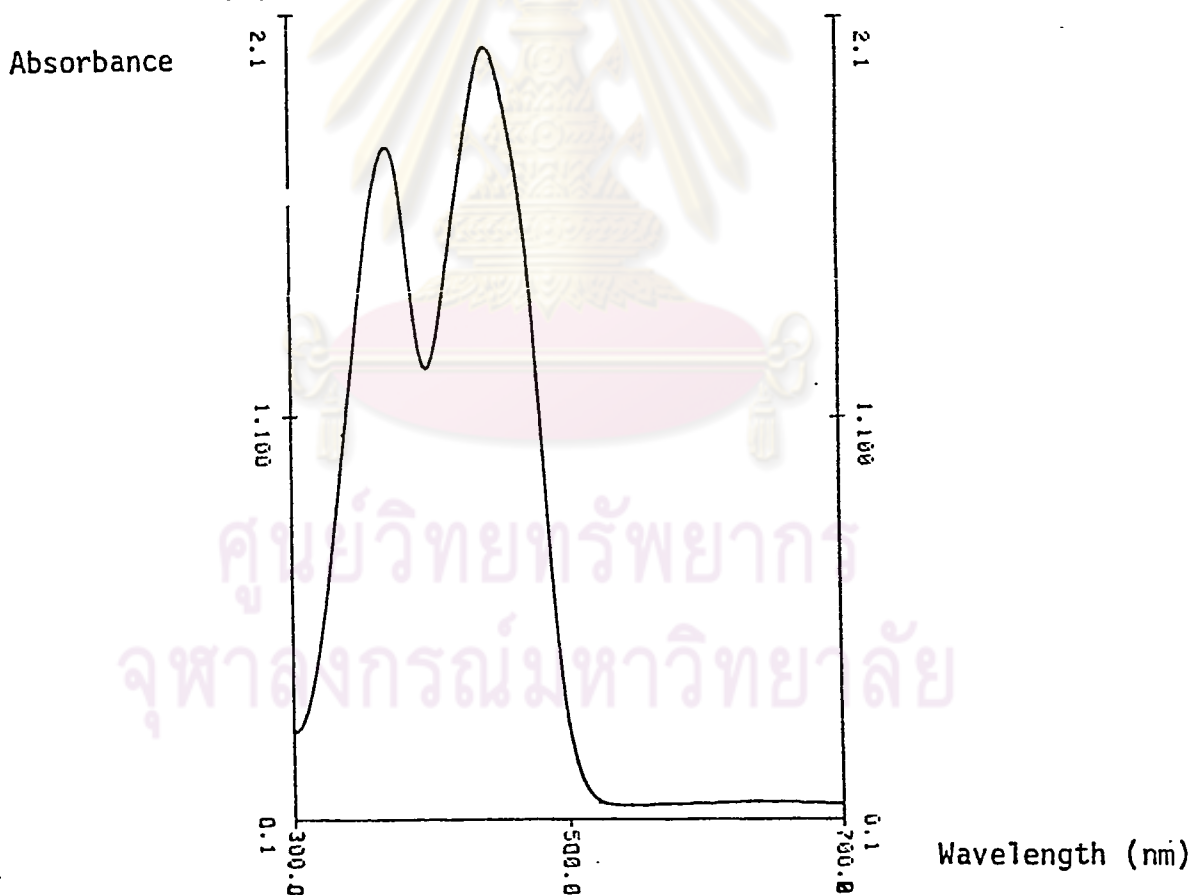


Figure 13. The absorption spectrum of riboflavin (pH 7.4).



Figure 14. The absorption spectrum of diethanolamine (pH 9.5).

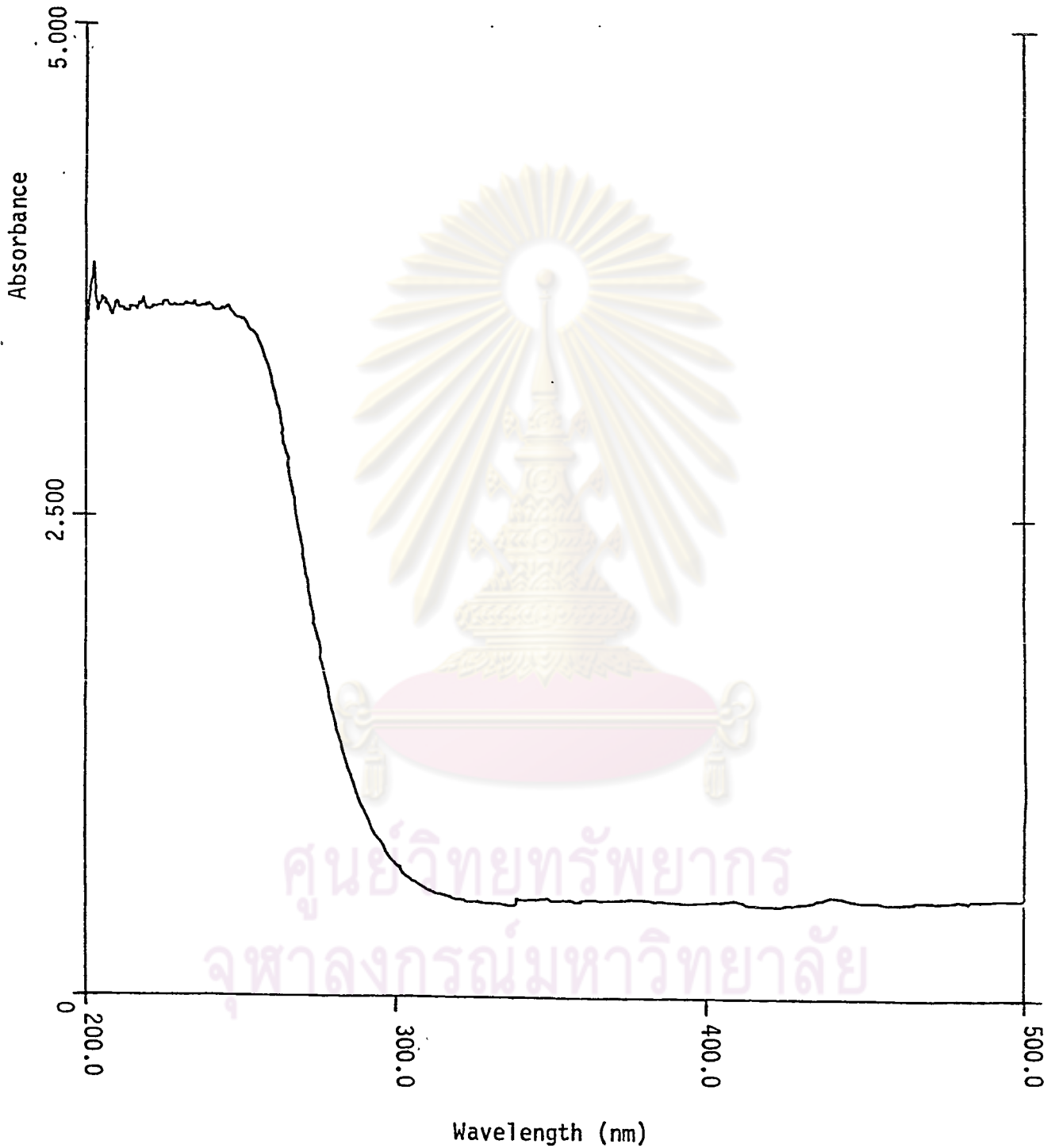


Figure 15. The absorption spectrum of the Pyrex cell (Glass no. 5510).

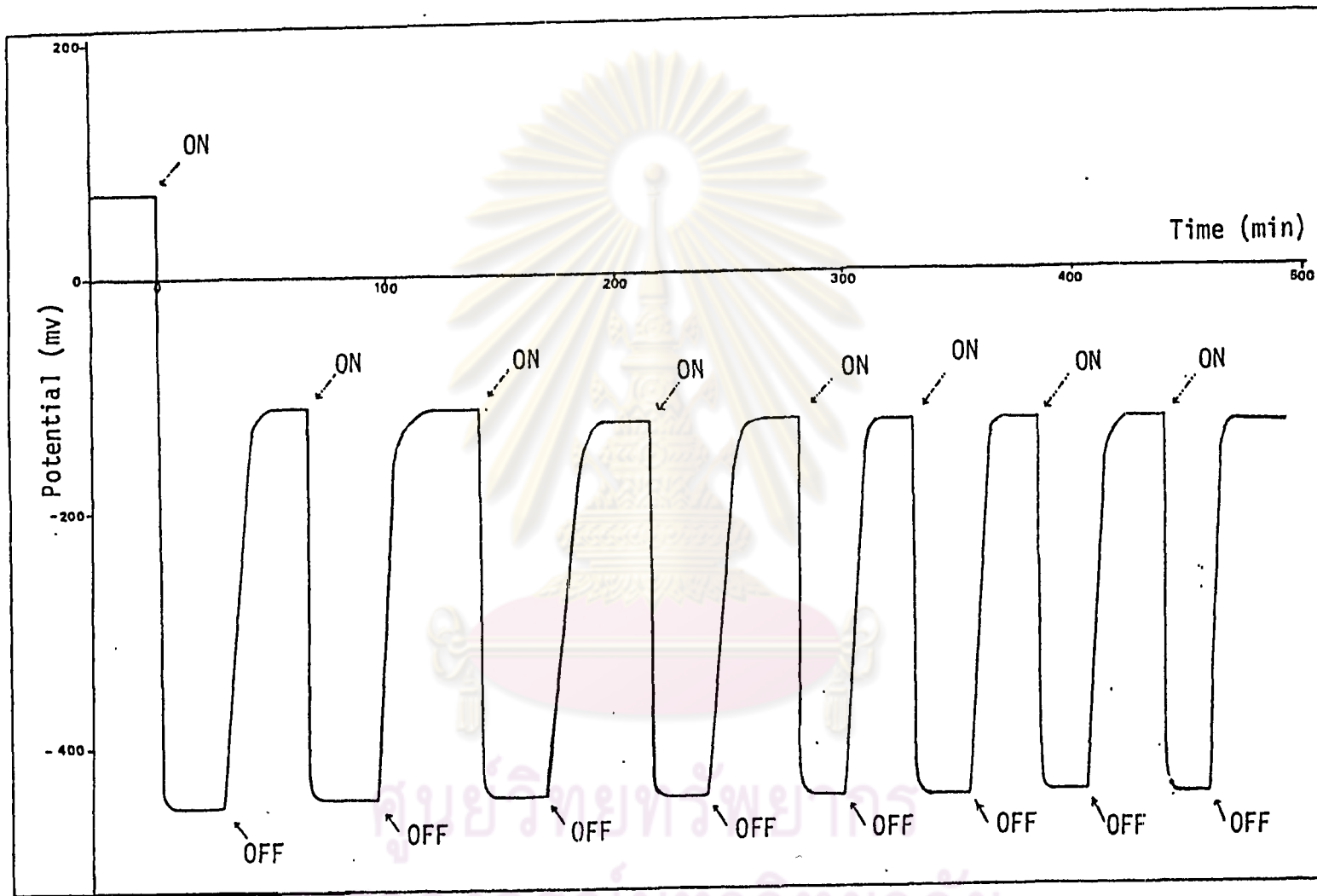
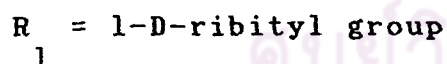
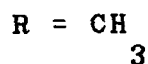
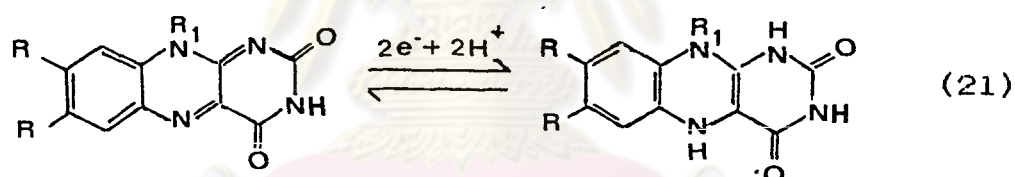


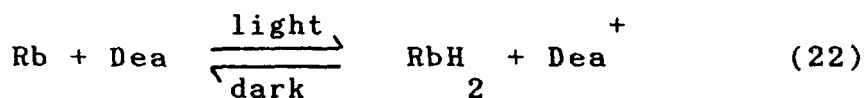
Figure 16. The potential behavior of the photogalvanic Rb-Dea system : $[Rb] = 1.2 \times 10^{-4}$ mol dm⁻³ ; $[Dea] = 2.5 \times 10^{-3}$ mol dm⁻³ ; pH 8.43.

potential decreased rapidly to the equilibrium value of approximately -450 mV within a few minutes, giving a maximum photopotential of 520 mV. When illumination was stopped, the potential gradually increased until an equilibrium value was, again, obtained but it did not recover to the initial value completely. These results suggest that the main reversible photochemical reaction is accompanied by some irreversible steps.

Riboflavin has been found to undergo reduction both in the presence and in the absence of a reducing agent (38). The reaction can be represented as:



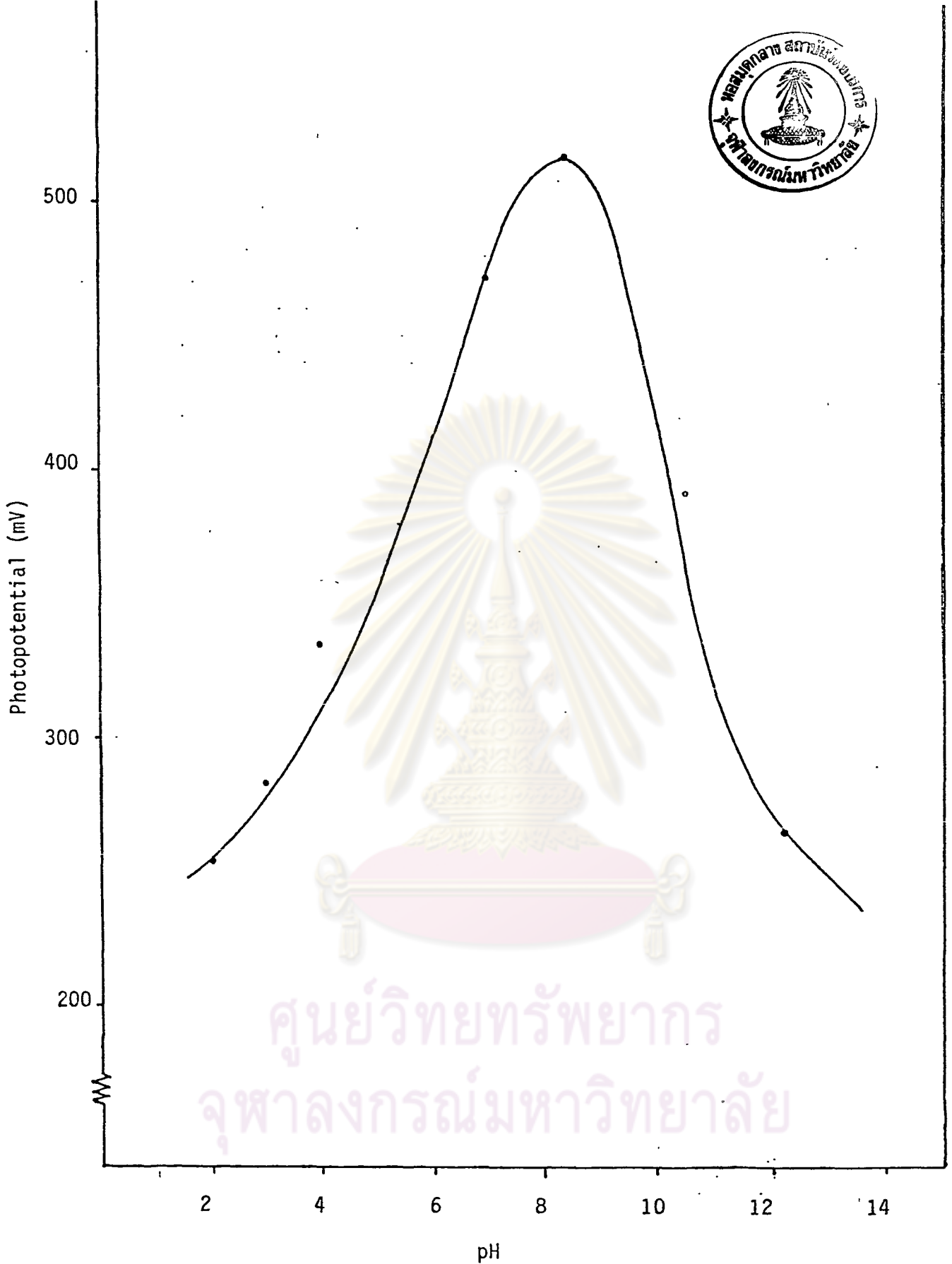
Under illumination, a solution of riboflavin or diethanolamine alone did not show any potential change. A photogalvanic cell has been developed (13) in which riboflavin is photoreduced by EDTA, giving a photopotential of 654 mV. It is believed that similar reactions i.e. photoreduction of riboflavin and simultaneous oxidation of diethanolamine occur in this system as shown :



The redox potential of riboflavin is -0.186 V at pH 7 and at 20°C (38) but that of diethanolamine is unknown. However, it may be predicted that redox potential of diethanolamine is greater than that of riboflavin because diethanolamine and riboflavin do not react in the dark.

- *Effect of pH.* The effect of solution pH on the photopotential is shown in Figure 17. It can be seen that the photopotential is maximum at pH 8.43. This result indicates that H^+ is involved in at least one of the elementary steps.

- *Effect of oxygen.* The effect of oxygen gas on photopotential are shown in Figure 18. If oxygen is introduced after the maximum potential value has been obtained (Figure 18 (a)), the potential immediately increases until the original value is reached within a minute. The result indicates that the photochemically-reduced species is more or less completely oxidized. Its effect is the same as what happens when illumination is stopped but oxygen has a more pronounced influence. This means that the reverse reaction (oxidation by oxygen) occurs at a rate much greater than that for the forward reaction (photoreduction of Rb). When oxygen is removed the system resumes its photostationary state close to the original one but the maximum photopotential slightly increases. The exact cause of this increase is unknown



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Figure 17. pH dependence of the photopotential of the Rb-Dea system : $[Rb] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[Dea] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$.

but it can be assumed that the equilibrium is now shifted a little further to the right (equation (22)). If illumination is stopped during the passage of oxygen, the potential of the system increases further (Figure 18(b)). It seems logical, then, to conclude that the equilibrium now lies far to the left and the dominant species in the solution may be different from those present originally.

Finally, the system is allowed to reach its stationary state in the dark after one illumination cycle and then purged with oxygen (Figure 18(c)). The potential rapidly changes back to the original value in the dark prior to illumination. At this point it is quite clear that any 'irreversible' step(s) in the reaction mechanisms can be made reversible by passage of oxygen gas. Furthermore, it can be seen that as long as the system is continuously purged with oxygen, any subsequent illumination will produce very little response. However, when oxygen is turned off, the typical photopotential response is again obtained.

- *Effect of temperature.* The variations of photopotential with temperature are shown in Figure 19. It can be seen that as the temperature of the dark compartment increases (the temperature of the illuminated compartment being maintained at 29 C), the photopotential remains virtually constant. Since the redox potential of calomel electrode is affected by temperature shown by the equation,

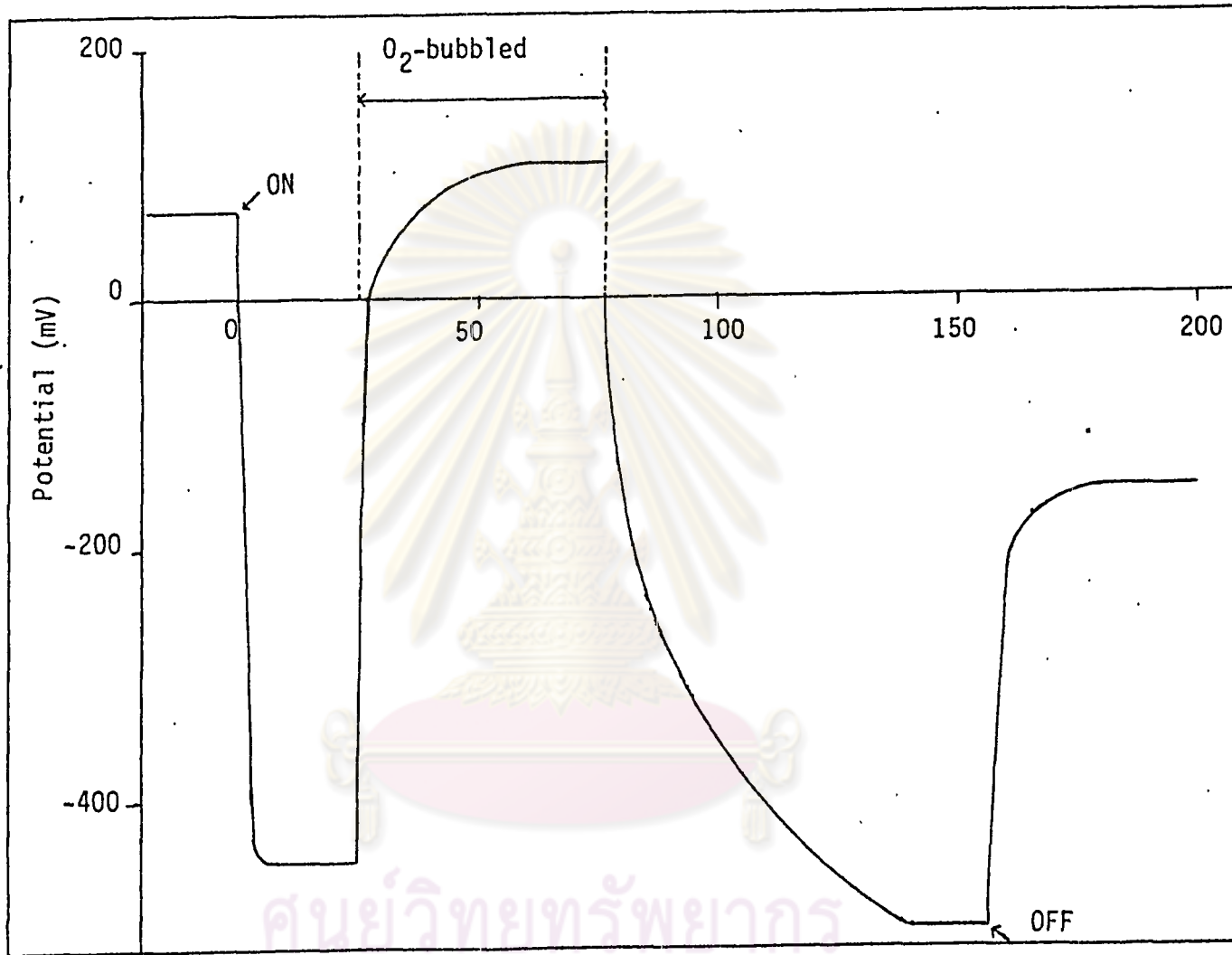


Figure 18. Effect of the oxygen gas on the photopotential of the Rb-Dea system : $[Rb] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[Dea] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$; pH 8.43 (a) oxygen bubbled during photostationary state.

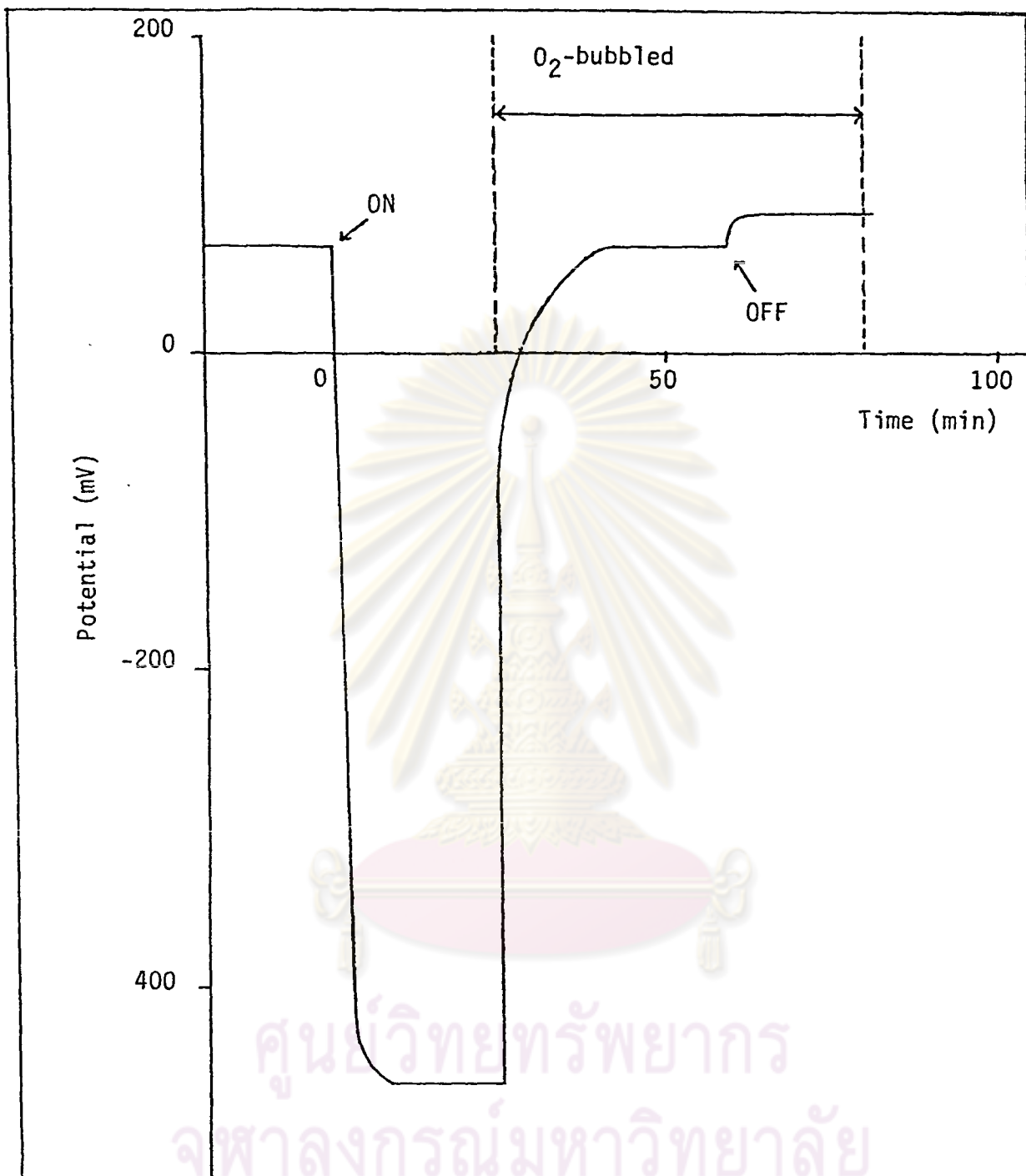


Figure 18. Effect of the oxygen gas on the photopotential of the Rb-Dea system : $[Rb] = 1.2 \times 10^{-4}$ mol dm⁻³ ; $[Dea] = 2.5 \times 10^{-3}$ mol dm⁻³ ; pH 8.43 (b) oxygen bubbled during and after illumination.

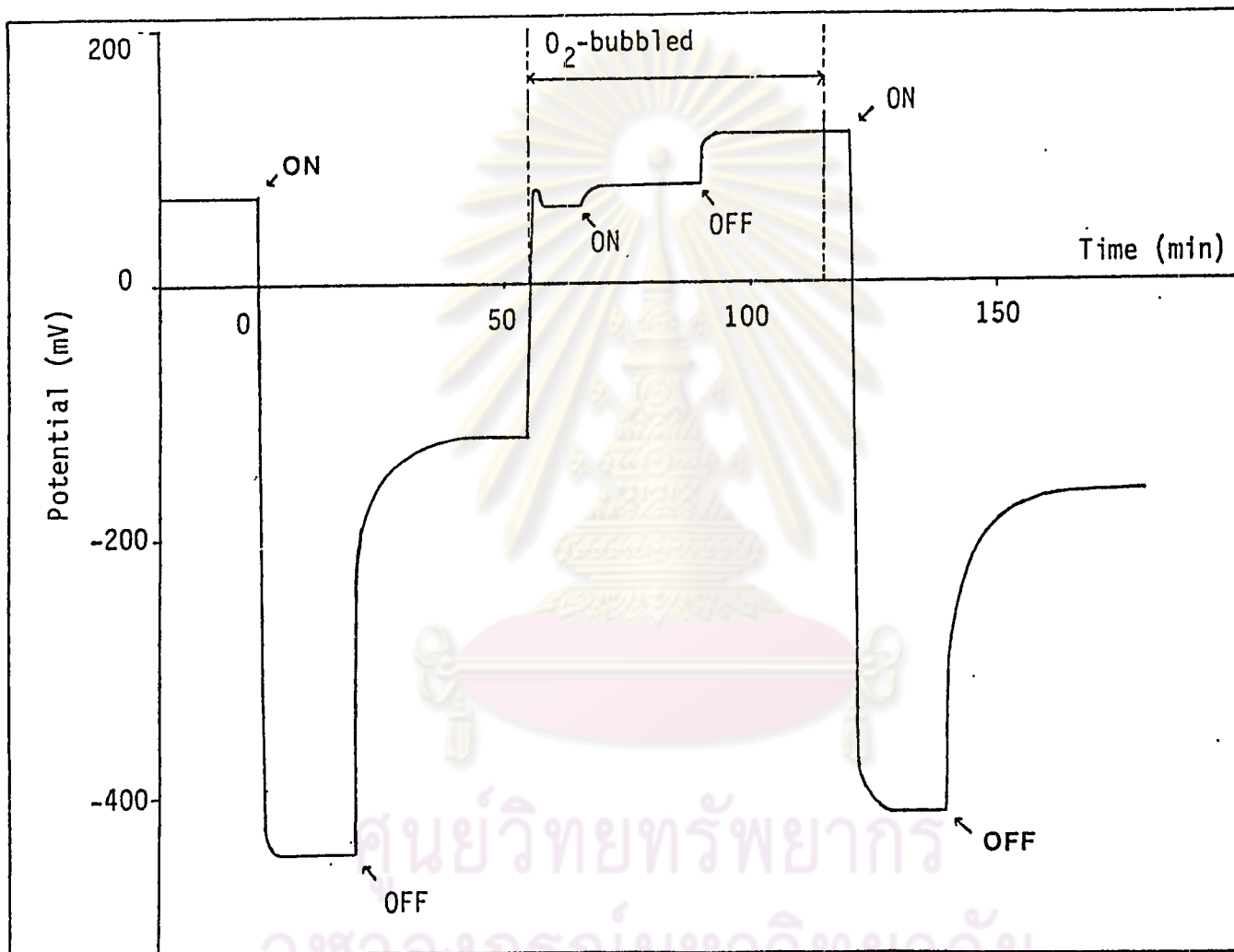


Figure 18. Effect of the oxygen gas on the photopotential of the Rb-Dea system : $[Rb] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[Dea] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$; pH 8.43 (c) oxygen bubbled after one illumination cycle.

$$E^{\circ} = 0.2800 - 2.4 \times 10^{-4} (t - 25^{\circ} \text{C}) \quad (23)$$

where t is temperature, the redox potential at different temperatures (29 to 80 °C) can be calculated. The results are shown in Table 4.

Table 4. The redox potentials (E°) of 1N calomel electrode at different temperatures.

Temperature (°C)	E° (V)
29	0.2790
40	0.2764
50	0.2740
60	0.2716
70	0.2692
80	0.2668

It can be seen that although the redox potential of calomel electrode decreases slightly as the temperature increases, the difference in potential between 29 °C (room temperature) and 80 °C is very small ($E_{29^{\circ} \text{C}}^{\circ} - E_{80^{\circ} \text{C}}^{\circ} = 0.0122 \text{ v}$). So, the potential of the system is only slightly affected by the increasing temperature of the dark compartment. This probably indicates that the position of equilibrium in the system is determined primarily by what goes on in the illuminated compartment and not in the dark compartment.

On the other hand, raising the temperature of the illuminated compartment, with the dark compartment maintained at constant 29 C, results in decrease in photopotential. The effect on the photopotential is mainly due to the influence of temperature on the photochemical steady state of the photogalvanic system. Thus, it has been found for the thionine-iron system (39) that at low temperatures the solution is completely bleached whereas this is not the case at higher temperatures. However, for the riboflavin-diethanolamine system no such effect was observed probably because the dye concentration was too high or the reverse reaction too fast for complete bleaching.

When the temperature of both compartments is simultaneously increased the photopotential follows the same trend as in the case of increasing only the temperature of the illuminated compartment. It may be concluded that the photogalvanic cell employing the riboflavin-diethanolamine system wherein either only the illuminated compartment or both compartments are maintained at a higher temperature may not be of much practical utility (due to the decreasing photopotential) whereas operation either with a higher temperature of the dark compartment or with the ambient temperature is beneficial. These results are similar to those for the thionine-iron system (39).

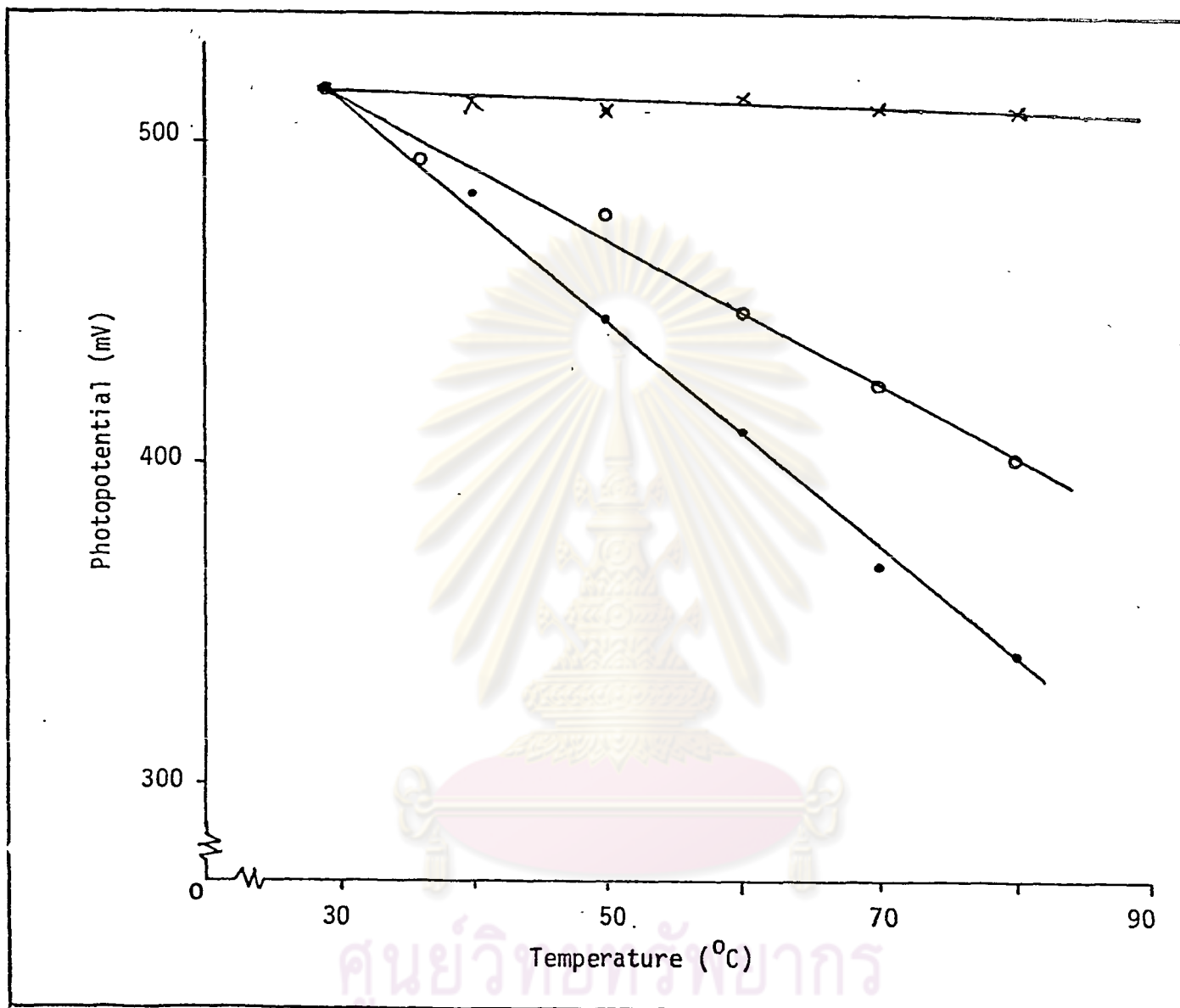


Figure 19. Variation of the photopotential of the Rb-Dea system with the temperature of the dark compartment (x), of the illuminated compartment (o), and of both compartments (●) : $[Rb] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[Dea] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$; pH 8.43.

- *Effect of organic solvents.* The effect of some water-soluble organic solvents on the photopotential of the Rb-Dea system is shown in Figures 20-23. Generally, when each organic solvent is introduced into the system after the photostationary state has been reached, the effect is to reduce the photopotential for a limited length of time (2-3 minutes). This reduction in photopotential, which is immediately followed by a more gradual increase to another equilibrium value, appears to be dependent on the amount of alcohol added, as shown in the case of isopropanol (Figure 24) and t-butanol (Figure 25). The final photopotential varies within the range 466 mV (for ethanol)- 534 mV (for isopropanol).

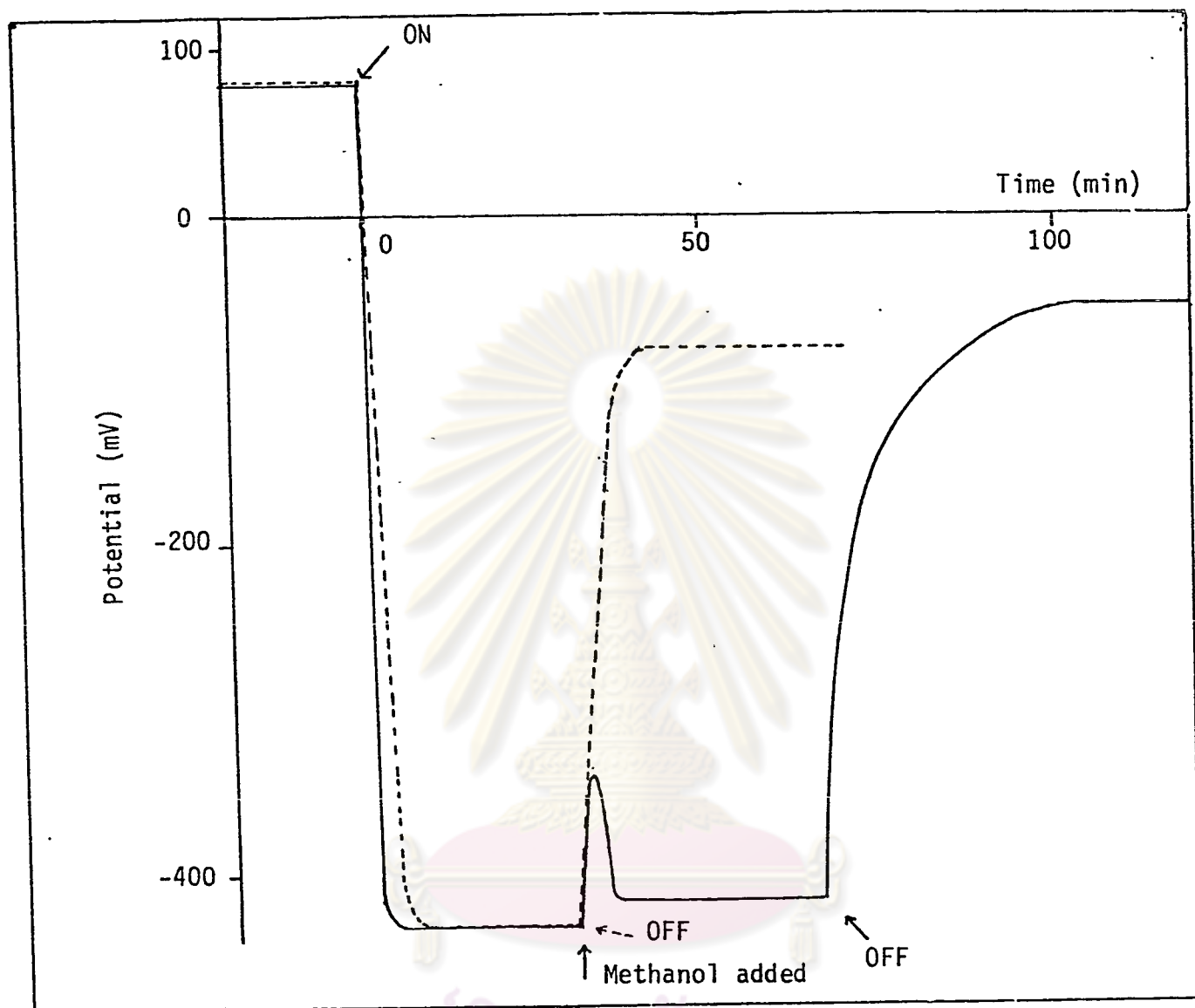
When each alcohol is added in the dark, however, the photopotential behavior resembles that for the original aqueous system except that the photopotential value is different-514, 492, 553 and 528 mV for methanol, ethanol, isopropanol and t-butanol, respectively.

Alcohol dissolved in the system in its photostationary state, especially in the vicinity of the electrode and in the region of light absorption, probably shifts the position of equilibrium by reacting with some species in solution, disturbing the process of light absorption, and interfering with the absorption/desorption process on the electrodes. The disturbances

are short-lived although the final photostationary state in each case is apparently different from the original one. Without detailed knowledge of the species present in solution and of the interactions between them, no definite conclusions can be drawn at this stage. The same applies to the results obtained from addition of alcohols in the dark.



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Figure 20. Effect of methanol (1.0 cm) on the photopotential of the Rb-Dea system: $[Rb] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[Dea] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$; pH 8.43

- methanol added during photostationary state
- - - methanol added in the dark

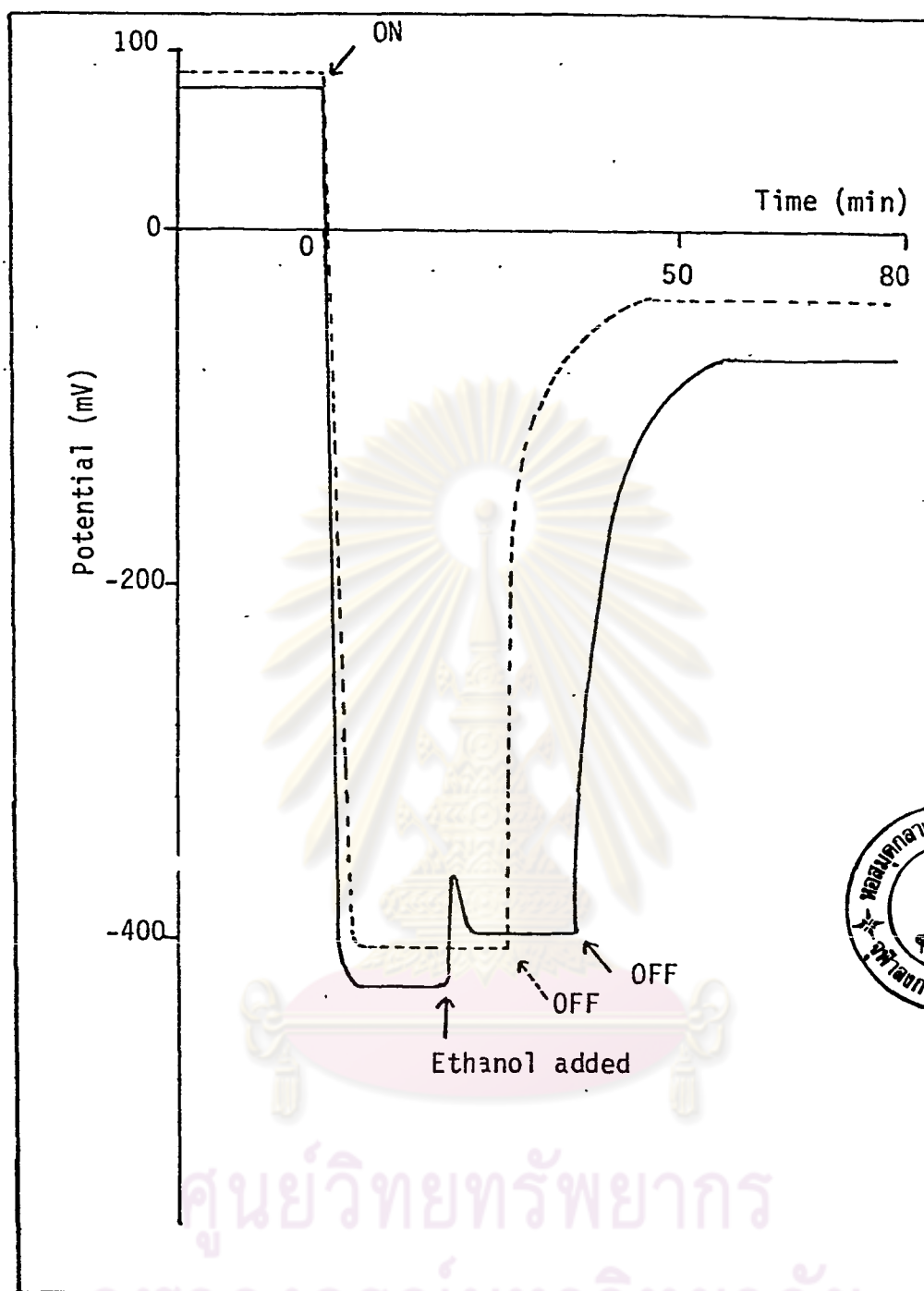


Figure 21. Effect of ethanol (1.0 cm) on the photopotential of the Rb-Dea system : $[Rb] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[Dea] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$; pH 8.43

- ethanol added during photostationary state
 - - - ethanol added in the dark

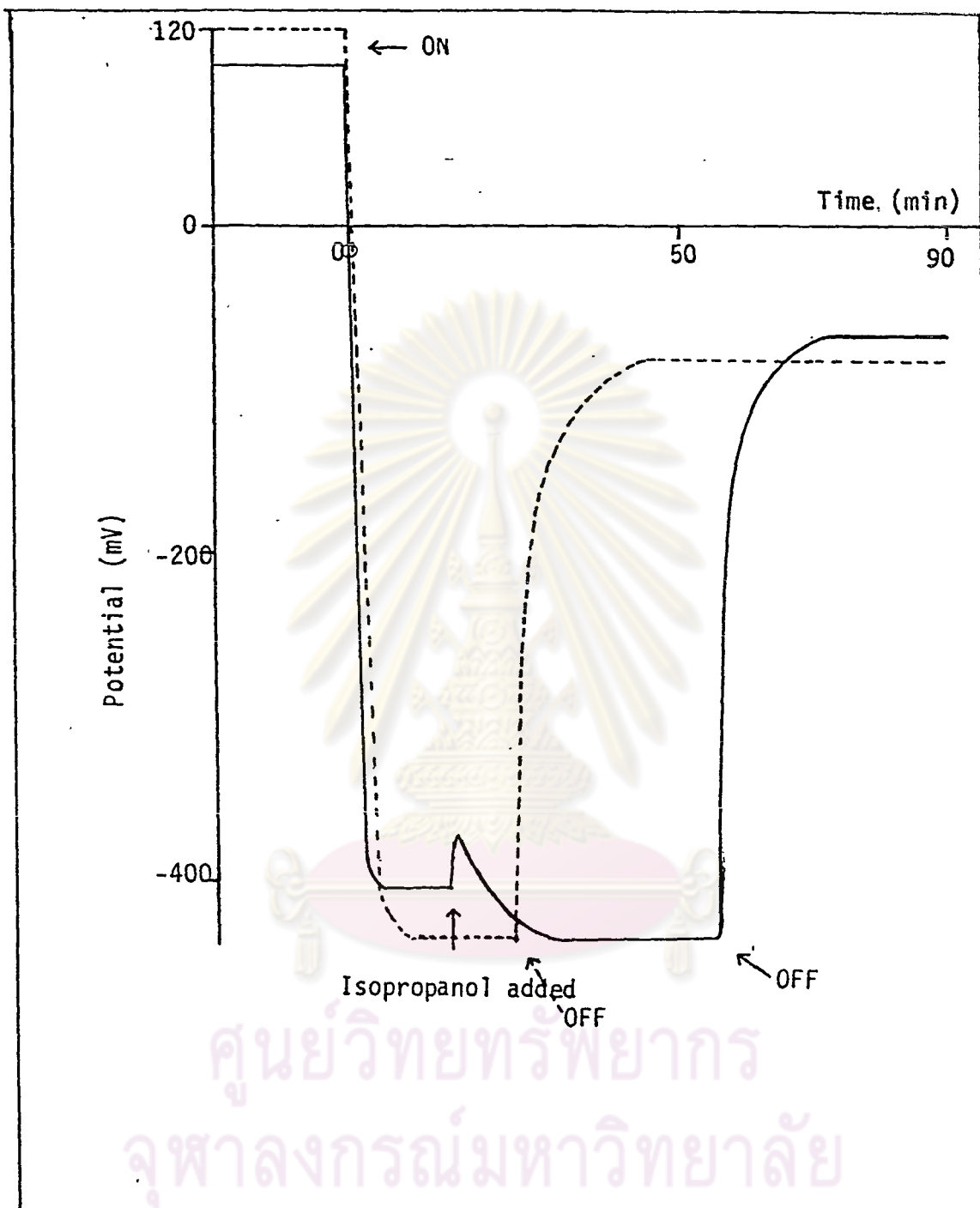


Figure 22. Effect of isopropanol (1.0 cm³) on the photopotential of the Rb-Dea system : [Rb] = 1.2×10^{-4} mol dm⁻³ ; [Dea] = 2.5×10^{-2} mol dm⁻³ ; pH 8.43

— isopropanol added during photostationary state
 - - - isopropanol added in the dark.

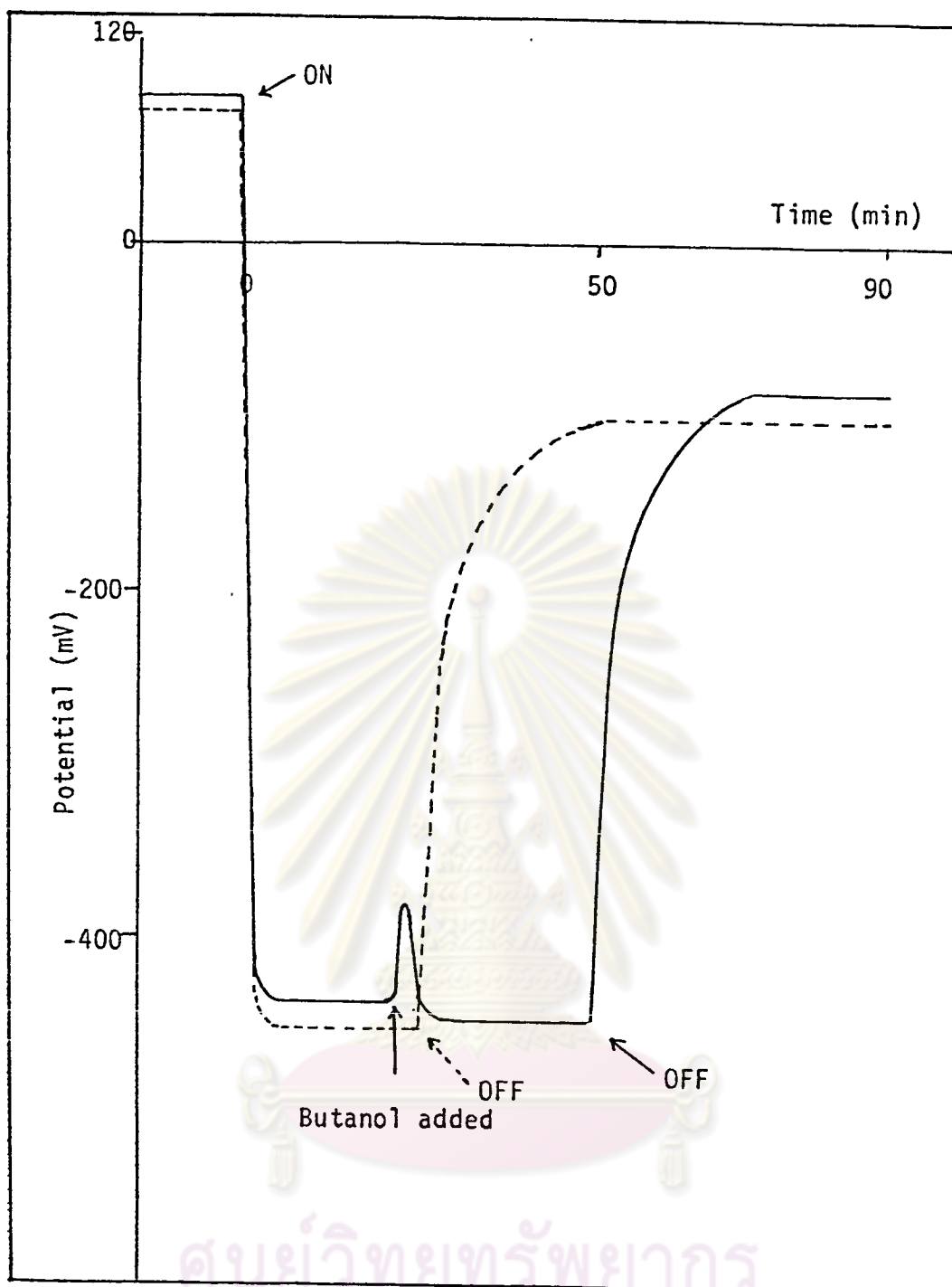


Figure 23. Effect of tert-butanol (1.0 cm^3) on the photopotential of the Rb-Dea system : $[\text{Rb}] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{Dea}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$; pH 8.43

— tert-butanol added during photostationary state

----- tert-butanol added in the dark.

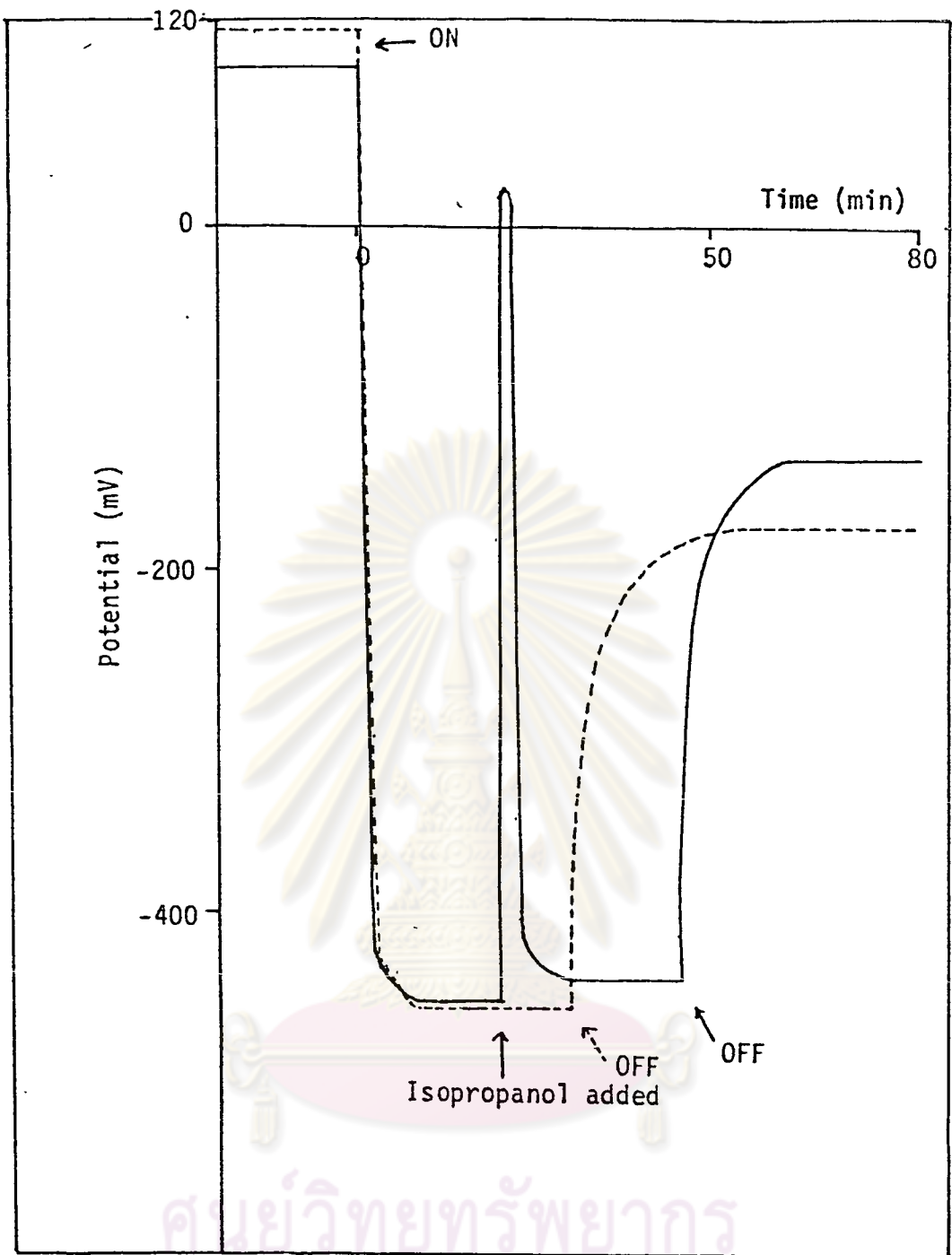


Figure 24. Effect of isopropanol (10.0 cm^3) on the photopotential of the Rb-Dea system : $[\text{Rb}] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{Dea}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$; pH 8.43

- isopropanol added during photostationary state
- - - isopropanol added in the dark.

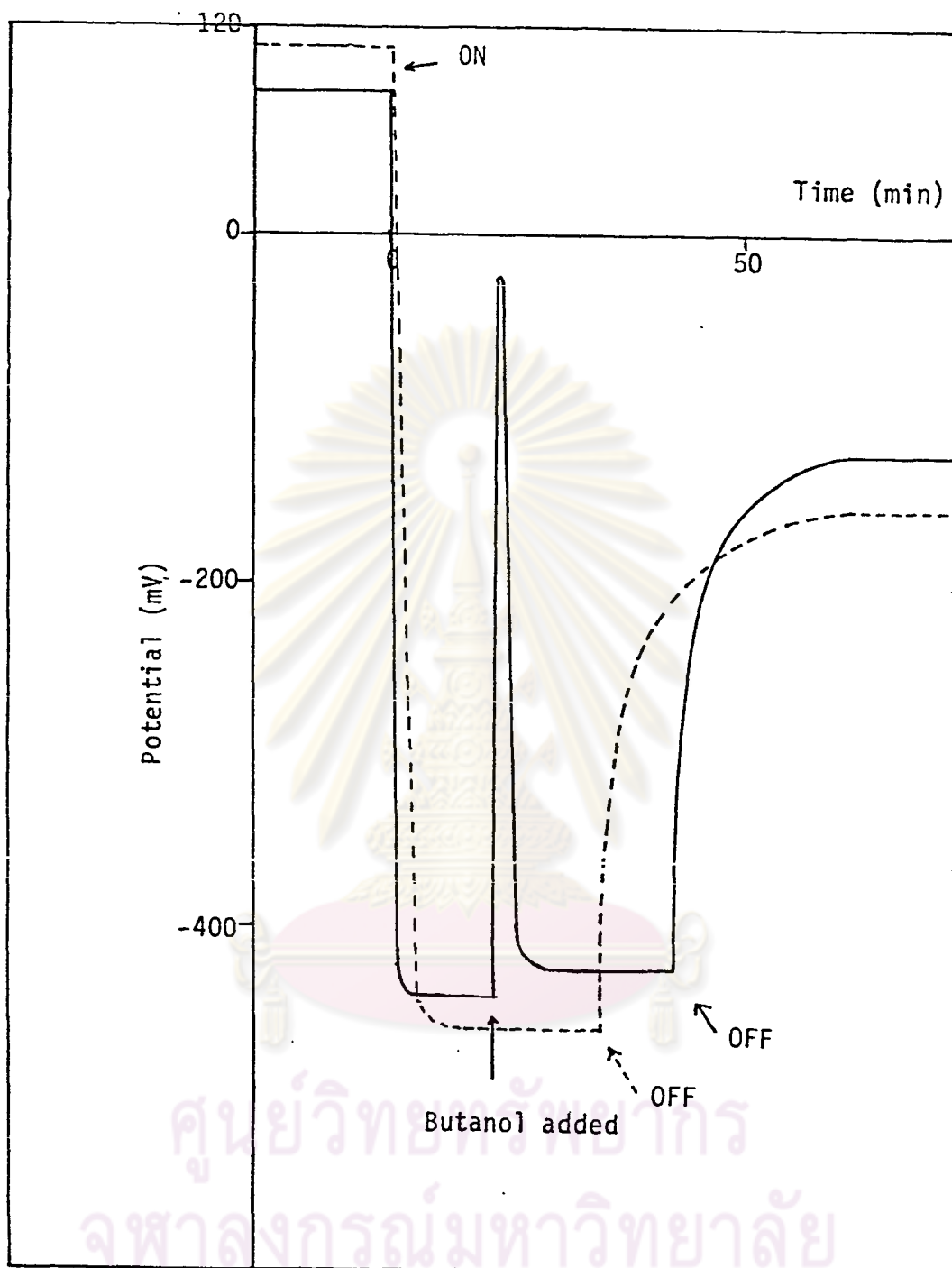


Figure 25. Effect of tert-butanol (10.0 cm^3) on the photopotential of the Rb-Dea system : $[\text{Rb}] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{Dea}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$; pH 8.43

- tert-butanol added during photostationary state
- tert-butanol added in the dark.

4.2.2 Photocurrent study

A typical pattern of photocurrent-time relationship of the Rb-Dea system is represented in Figure 26. At the beginning there is a sharp decrease in photocurrent as soon as illumination starts until a maximum value (PC_{max}) is reached. This is followed by a more gradual increase to an equilibrium value (PC_{eq}) within a few minutes. When the light source is turned off, the current increases to a value close to that prior to illumination. The current-time curve may be thought of as consisting of two components - a fast negative response (i_-) and a subsequent - positive response (i_+) as shown. The relationship between i and PC is obvious :

$$i_- = \left| PC_{max} \right| ; \quad i_+ = \left| PC_{max} - PC_{eq} \right|$$

For the thionine-iron system it has been reported (37) that the active species at the electrodes are the semidye and the ferric ion, but the mechanism for the Rb-Dea system is still unknown. The following is an attempt to elucidate the reaction mechanism occurring in this system.

To identify the electrode active species, i.e. the chemical species donating an electron to the electrode or accepting one from it, the following consideration leads to the possible case.

Diethanolamine cannot be the active species in the light compartment because it cannot absorb visible

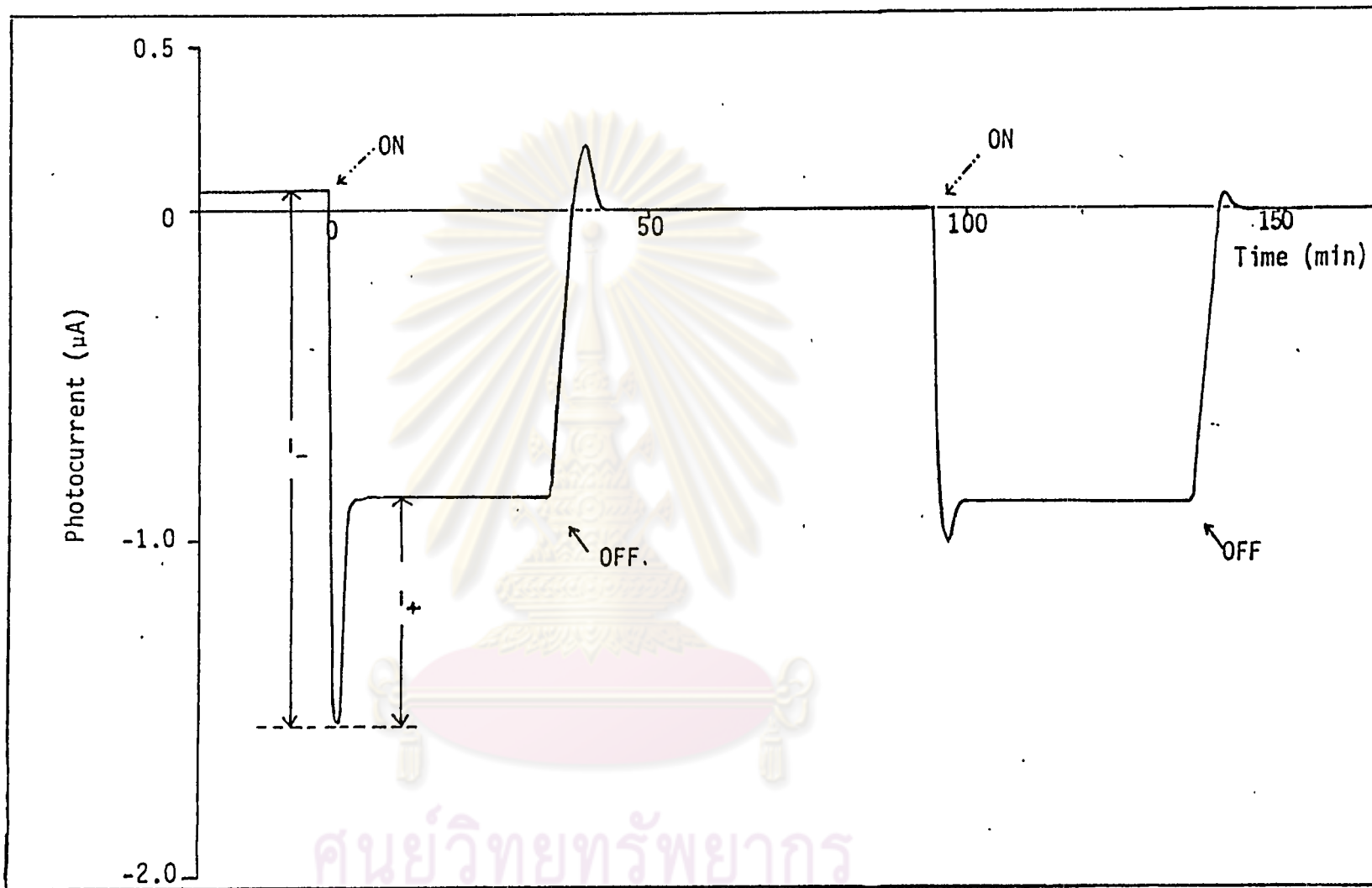


Figure 26. Photocurrent behavior of the Rb-Dea system : $[Rb] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[Dea] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$; pH 8.43; diffusion length = 14.6 cm.

light. Also, in the light compartment, most of the riboflavin should be in the reduced form and thus riboflavin is not likely to be the active species at the electrode in this compartment. For a similar reason it is unlikely that diethanolamine in its more abundant oxidized form will donate another electron to the illuminated electrode.

The only probable choice for the main active species at the illuminated electrode is the reduced form of riboflavin. So, the negative component of the photocurrent (i_{-}) is attributed to electron transfer from reduced riboflavin in the vicinity of the illuminated electrode to the electrode. The positive response could then be attributed to electron transfer from the dark electrode to some active species in the dark compartment. From the four possible cases (Table 5), two (1 and 2) can be rejected since RbH and Dea cannot be the main active species accepting an electron from the dark electrode.

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Table 5. Four possible cases for the electrode-active species in the Rb-Dea system.

Case	Electrode active species	
	Light compartment	Dark compartment
1	RbH 2	RbH 2
2	RbH 2	Dea
3	RbH 2	Rb +
4	RbH 2	Dea

Dea = diethanolamine

Rb = riboflavin

Dea⁺ = oxidized diethanolamine

RbH₂ = reduced riboflavin

In order to identify the active species at the dark electrode, the diffusion length of the photoreaction species between 2 electrodes was varied and the effect on the maximum and equilibrium photocurrents was observed. The results obtained are shown in Figure 27.

The values of PC_{max} and PC_{eq} are seen to be roughly independent of the diffusion length. The main

electron-accepting species in the dark compartment could either be the oxidized form of diethanolamine (Dea^+) or riboflavin (Rb) itself. If Dea^+ , which is produced only near the illuminated electrode is assumed to be the active species, it will have to diffuse to the dark electrode to accept an electron and PC_{eq} will then be inversely proportional to the diffusion length. This was in contradiction to the results shown in Figure (27). On the other hand, if Rb is the active species, then PC_{eq} would be more or less independent of the diffusion length, as found experimentally. Thus case 4 must be rejected and only case 3 is the most possible. It is, therefore, concluded that the main active species at the dark and illuminated compartments are riboflavin (Rb) and its reduced form (RbH_2), respectively. Photocurrent generation could then be described as in Figure 28. The reducing agent, Dea, and its oxidized compound behave as electron carriers diffusing through the path from the light to the dark compartment. The proposed mechanism of this redox system is similar to that of the SAF-EDTA system (14) but different from that of thionine-iron system in which the active species in the dark compartment is believed to be ferric ion i.e. the oxidized form of the reducing agent (37).

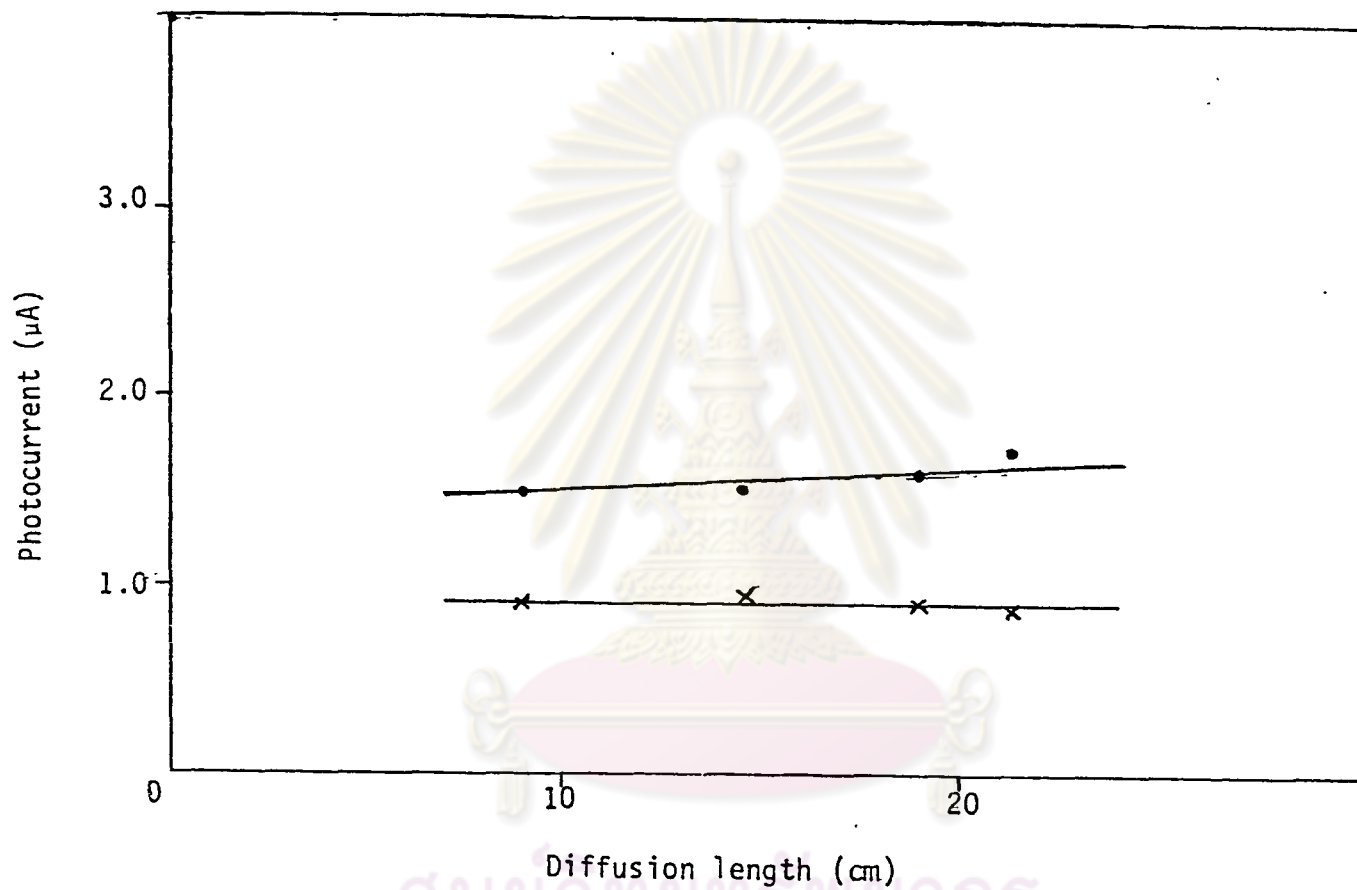


Figure 27. Effect of diffusion length between electrodes on PC_{max} and PC_{eq} : $[Rb] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[Dea] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$; pH 8.43 ; (o) PC_{max} ; (x) PC_{eq} .

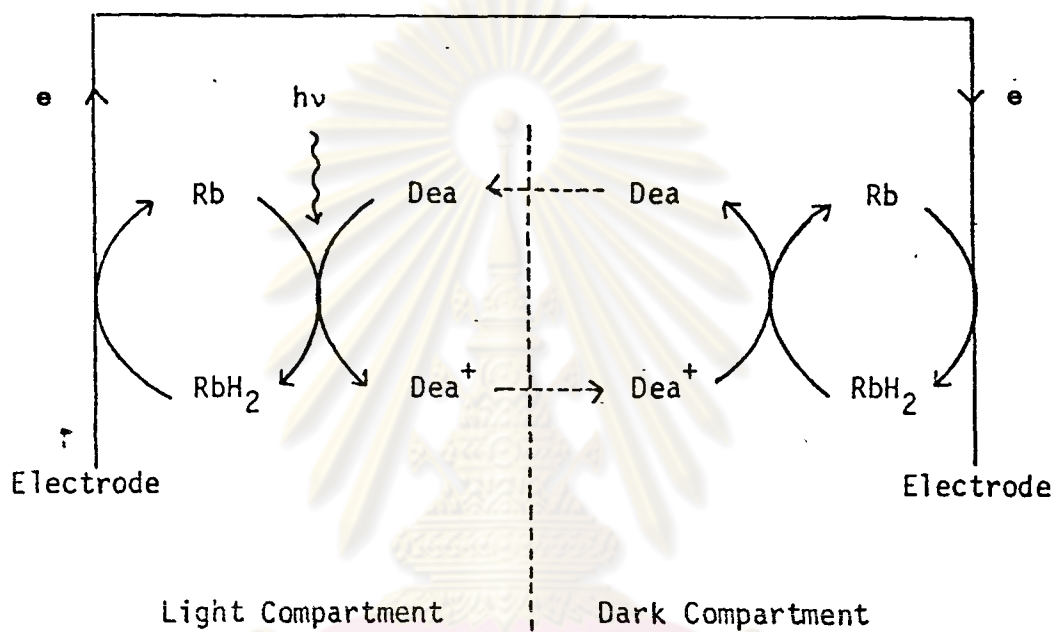


Figure 28. Reaction scheme for photocurrent generation of Rb-Dea system.

- *Effect of oxygen gas.* The results of oxygen gas bubbling through only the dark compartment, the illuminated compartment, and both compartments while measuring the photocurrent are shown in Figure 29 a, b, and c, respectively. Its effect can be the confirmation of the proposed reaction scheme very well. With oxygen bubbling through the illuminated compartment (Figure 29 (b)), i_+ and i_- are essentially zero. In other words, the system does not respond to the on-off illumination cycle. This may be due to either or both of the following:

(i) oxidation of Dea, leading to a decrease in Dea concentration in the vicinity of the illuminated electrode and, consequently, a decrease in concentration of photochemically-produced RbH_2 and

(ii) oxidation of photochemically-produced RbH_2 . Electron transfer to the electrode is then greatly reduced. On the other hand, bubbling oxygen through only the dark compartment (Figure 29 (a)) leads to a slight increase in both i_+ and i_- and a large increase in i_+ , indicating that electron transfer from RbH_2 to the illuminated electrode is little affected by oxygen in the dark compartment while electron transfer from the dark electrode to Rb is much enhanced by oxidation of RbH_2 to Rb. It is not surprising, therefore, that flushing both compartments simultaneously with oxygen, gave

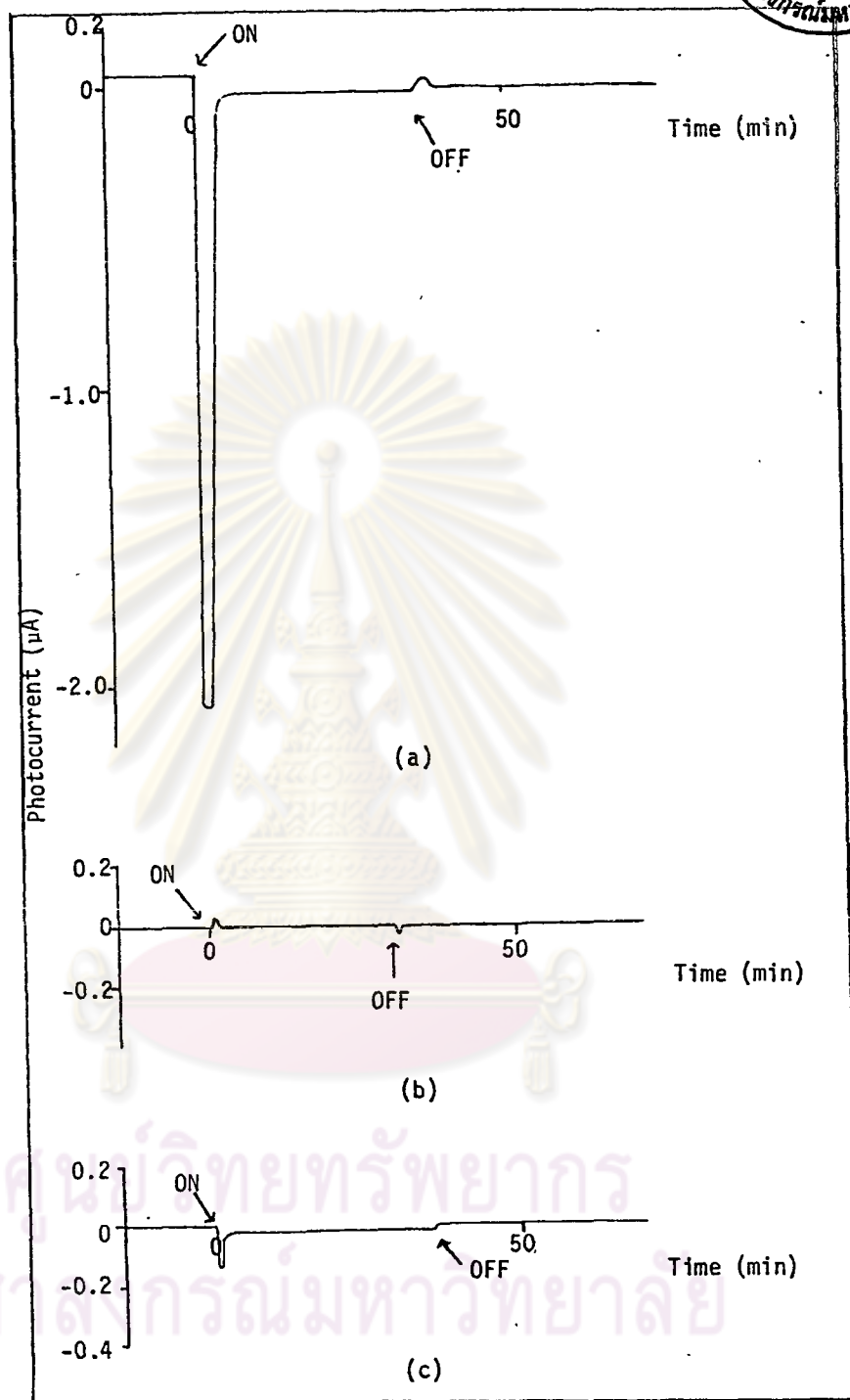


Figure 29. Effect of oxygen gas on the photocurrent of the Rb-Dea system: $[Rb] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[Dea] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$; pH 8.34.

- (a) oxygen bubbled through the dark compartment
- (b) oxygen bubbled through the illuminated compartment
- (c) oxygen bubbled through both compartments

intermediate results - a decrease in both i_- and i_+ (Figure 29 (c)).

- *Effect of temperature.* The results on the temperature effect are summarized in Tables 6, 7 and 8. For the temperature variation of the dark compartment, with the illuminated compartment maintained at a constant temperature of 29 C, the positive component of the photocurrent (i_+) slightly increases (Table 6). The relationship between photocurrent (i_+) and temperature is shown in Figure 30. Since the photocurrent i_+ is associated with the active species at the dark electrode (Rb), it may be possible that higher temperatures increase the mobility of Rb (and Dea) in the dark compartment. Hence, the rate at which Rb accepts an electron from the electrode is increased, resulting in a higher i_+ value. Meanwhile, although the temperature of the illuminated compartment was kept reasonably constant at room temperature during the experiment, a temperature gradient existed between the two compartments and convection in solution was inevitable. Under such conditions, the rate at which Dea moves from the dark compartment to the other (in order to reduce photoexcited Rb) should be expected to be higher, due to a consequent increase in $[RbH_2]$. This probably explains why higher values of i_- were also obtained (Figure 31) since a higher RbH_2 concentration implies a higher rate of electron transfer to the illuminated electrode.

Table 6. Effect of the temperature variation in the dark compartment of the Rb-Dea system.*

Temperature							
(μ A)	($^{\circ}$ C)	29	40	50	60	70	80
Photocurrent							
$i = \left \begin{array}{c} \text{PC} \\ - \\ \text{max} \end{array} \right $		1.85	2.15	2.55	3.25	3.90	4.25
PC		-0.85	-1.45	-1.58	-1.65	-1.95	-1.90
$i = \left \begin{array}{cc} \text{PC} & -\text{PC} \\ + & \text{max} \quad \text{eq} \end{array} \right $		1	0.7	0.97	1.65	1.95	2.35

Table 7. Effect of the temperature variation in the illuminated compartment of the Rb-Dea system.*

Temperature							
(μ A)	($^{\circ}$ C)	29	36	50	60	70	80
Photocurrent							
$i = \left \begin{array}{c} \text{PC} \\ - \\ \text{max} \end{array} \right $		1.85	3.80	10.10	12.30	17.20	20.10
PC		-0.85	-1.05	-1.40	-1.45	-1.15	-1.05
$i = \left \begin{array}{cc} \text{PC} & -\text{PC} \\ + & \text{max} \quad \text{eq} \end{array} \right $		1	2.75	8.7	10.85	16.05	19.05

Table 8. Effect of the temperature variation in both compartments of the Rb-Dea system.*

temperature							
(μ A)	($^{\circ}$ C)	29	40	50	60	70	80
Photocurrent							
$i = \left \begin{array}{c} \text{PC} \\ - \\ \text{max} \end{array} \right $		1.85	5.0	7.35	9.55	12.40	-
PC		-0.85	-1.43	-1.95	-1.93	-1.95	-
$i = \left \begin{array}{cc} \text{PC} & -\text{PC} \\ + & \text{max} \quad \text{eq} \end{array} \right $		1	3.57	5.40	7.62	10.45	-

* [Rb] = 1.2×10^{-4} mol dm⁻³ ; [Dea] = 2.5×10^{-3} mol dm⁻³ ; pH 8.43; diffusion length = 21.3 cm.

The effect of temperature variation in the illuminated compartment, with the dark compartment maintained at a constant temperature of 29 °C is summarized in Table 7. In this case, i_+ and i_- show an approximately 20-fold increase in the temperature range 30 - 80 °C (Figures 30, 31), substantiating an earlier conclusion that the reaction mechanism is determined mainly by the detailed interactions of species in the illuminated compartment. An elevated temperature means a higher rate at which RbH_2 encounters the electrode and thus a higher rate of electron transfer. At the same time, thermal convection permits Dea^+ to move to the dark side much more efficiently. This, in turn, aids the conversion of RbH_2 to Rb and consequently helps to increase the rate at which Rb abstracts electrons from the dark electrode.

Finally, when the temperature of both compartments are simultaneously elevated, changes in i_+ and i_- are found to be intermediate between the first two cases (Table 8). Both i_- and i_+ increase approximately ten folds.

Although temperature elevation results in higher mobility for active species in solution, a greater ohmic loss is nevertheless inevitable, owing to a greater number of collisions. Apparently, when the temperature of any one of the compartments is raised, the effect on

mobility more than compensates for the increased ohmic loss. However, with both compartments at a higher temperature, ohmic loss may become quite considerable. It is not surprising, therefore, that i_+ and i_- values in Table 8 are slightly lower than those in Table 7.



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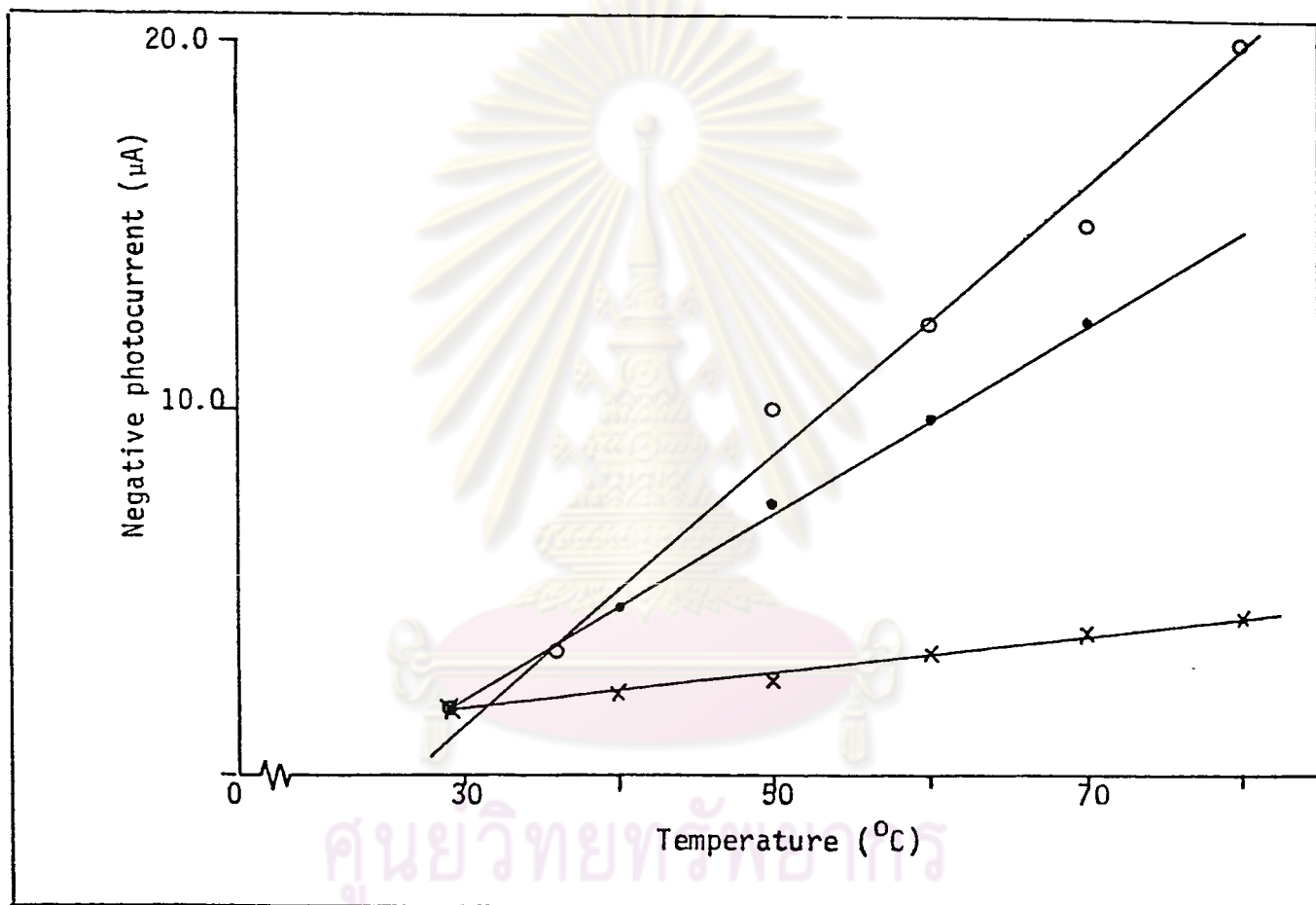


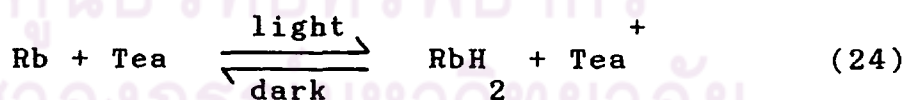
Figure 31. Variation of the negative component of the photocurrent (i) with the temperature of the dark compartment (x), of the illuminated compartment (o), and of both compartments (•)
 $[Rb] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[Dea] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$; pH 8.43.

4.3 The Riboflavin-Triethanolamine (Tea) System

Triethanolamine ((OHCH₂CH₂)₃N), like diethanolamine, has no absorption in the visible but absorbs in the ultraviolet region (Figure 32). Studies on the photopotential and photocurrent behavior of the Rb-Tea system parallel those made on the Rb-Dea system. Results will thus be discussed in terms of comparison between the two systems.

4.3.1 Photopotential study

The potential responses of the system to illumination cycles under optimum conditions ($[Rb] = 1.2 \times 10^{-4}$ mol dm⁻³; $[Tea] = 1.0 \times 10^{-2}$ mol dm⁻³; pH = 7.90) are shown in Figure 33. The dark potential is approximately -30 mV. Sensitivity to light is comparable to that of the Rb-Dea system, the photostationary state of potential -460 mV being attained within a few minutes. The photopotential (430 mV), however, is considerably lower, indicating that equilibrium of the reaction



where Tea stands for the oxidized form of triethanolamine, is not carried as far to the right as in its Dea counterpart. Another discrepancy between the two systems is that the Rb-Tea system shows an apparently better reversibility. When the light source is turned off the system shifts back to an equilibrium state for which the

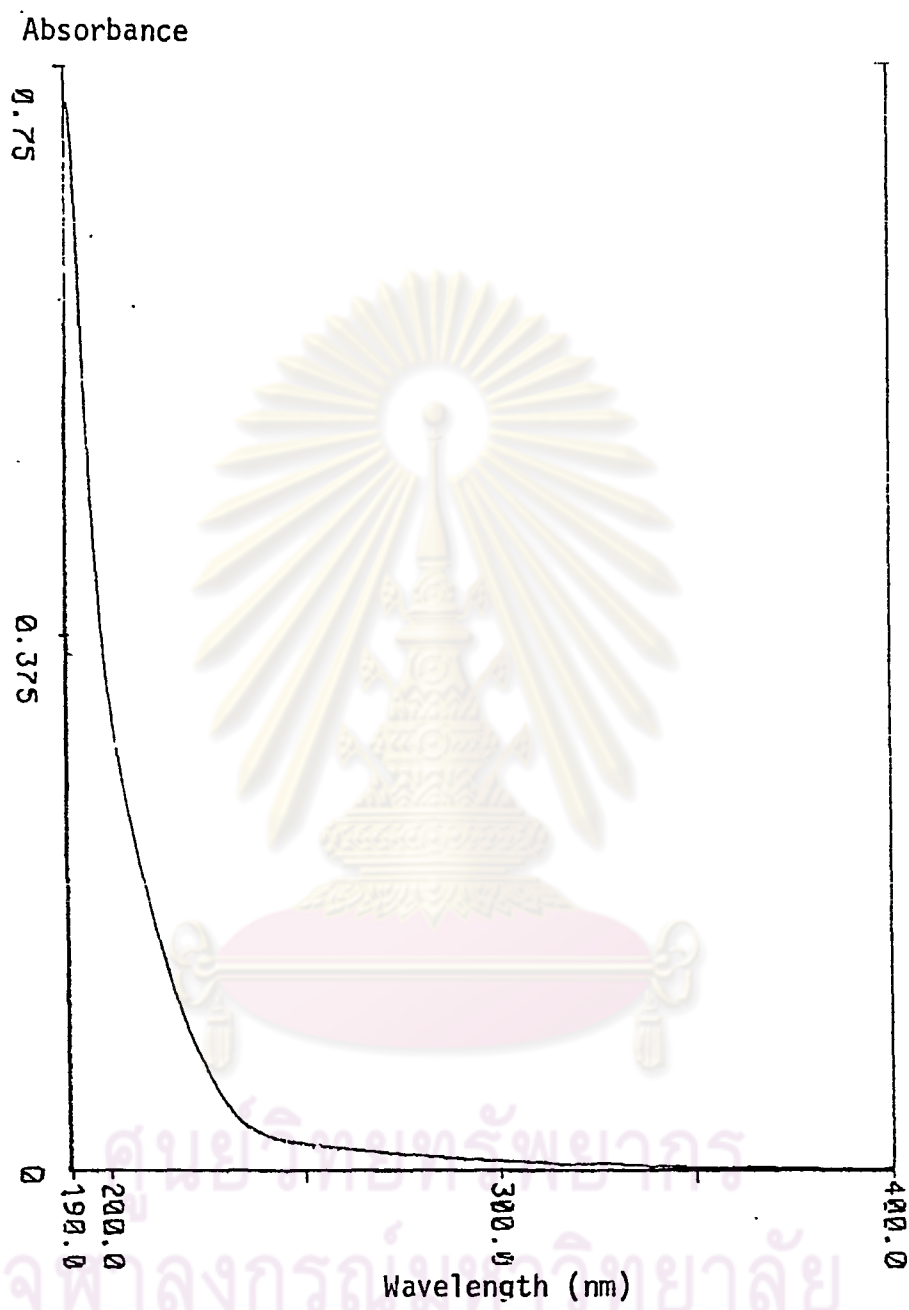


Figure 32. The absorption spectrum of triethanolamine (pH 8.7).

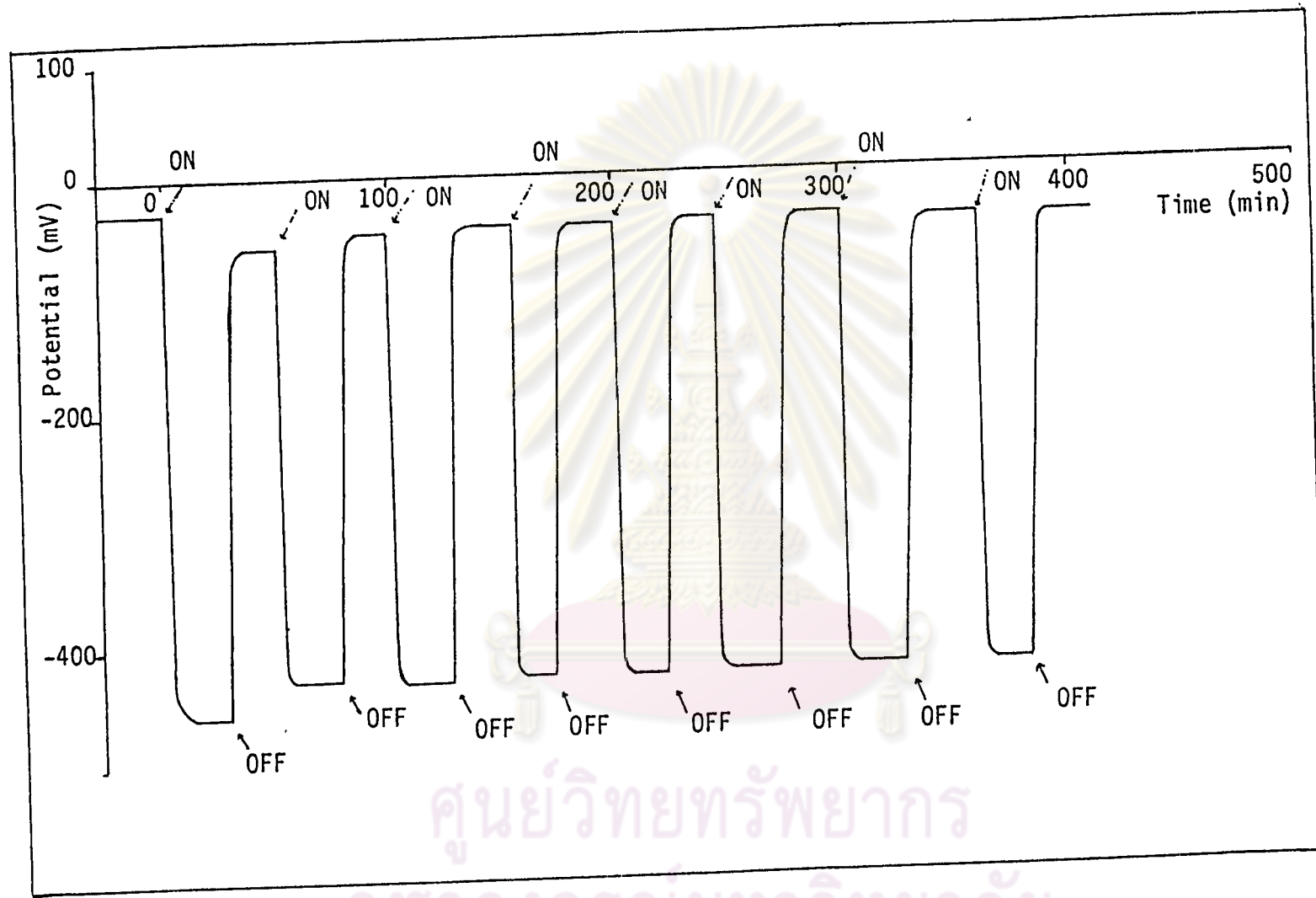


Figure 33. The potential behavior of the photogalvanic Rb-Tea system : $[Rb] = 1.2 \times 10^{-4}$ mol dm⁻³ ; $[Tea] = 1.0 \times 10^{-3}$ mol dm⁻² ; pH 7.90.

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potential with respect to the calomel electrode is almost exactly the same as the original dark potential. This potential - time behavior did not show any significant change after several illumination cycles. Since diethanolamine and triethanolamine are expected to be chemically similar, it seems reasonable to assume that the reduction potential of the Tea /Tea⁺ couple is much higher than that of the Rb/RbH₂ couple. During the course of illumination, riboflavin is photoreduced to RbH₂ while Tea is converted into Tea⁺. The assumed similarity between reactions in the two systems is also justified by the fact that the pH value at maximum photopotential (ca. 7.90, Figure 34) is close to the value obtained previously for the Rb-Dea system.

As in the case for triethanolamine, introduction of oxygen into the system in its photostationary state rapidly shifts the equilibrium to the left and a potential close to the dark potential is again obtained although the system is still under illumination (Figure 35 (a)). Evidently, oxidation by oxygen occurs at a greater rate compared with photoreduction of riboflavin. This result is the same as what has been found experimentally for the Rb-Dea system (Figure 18 (a)). However, when the supply of oxygen is turned off, only about half of the photopotential is readily recovered, indicating production of some stable oxidation product which was probably absent before oxygen introduction.

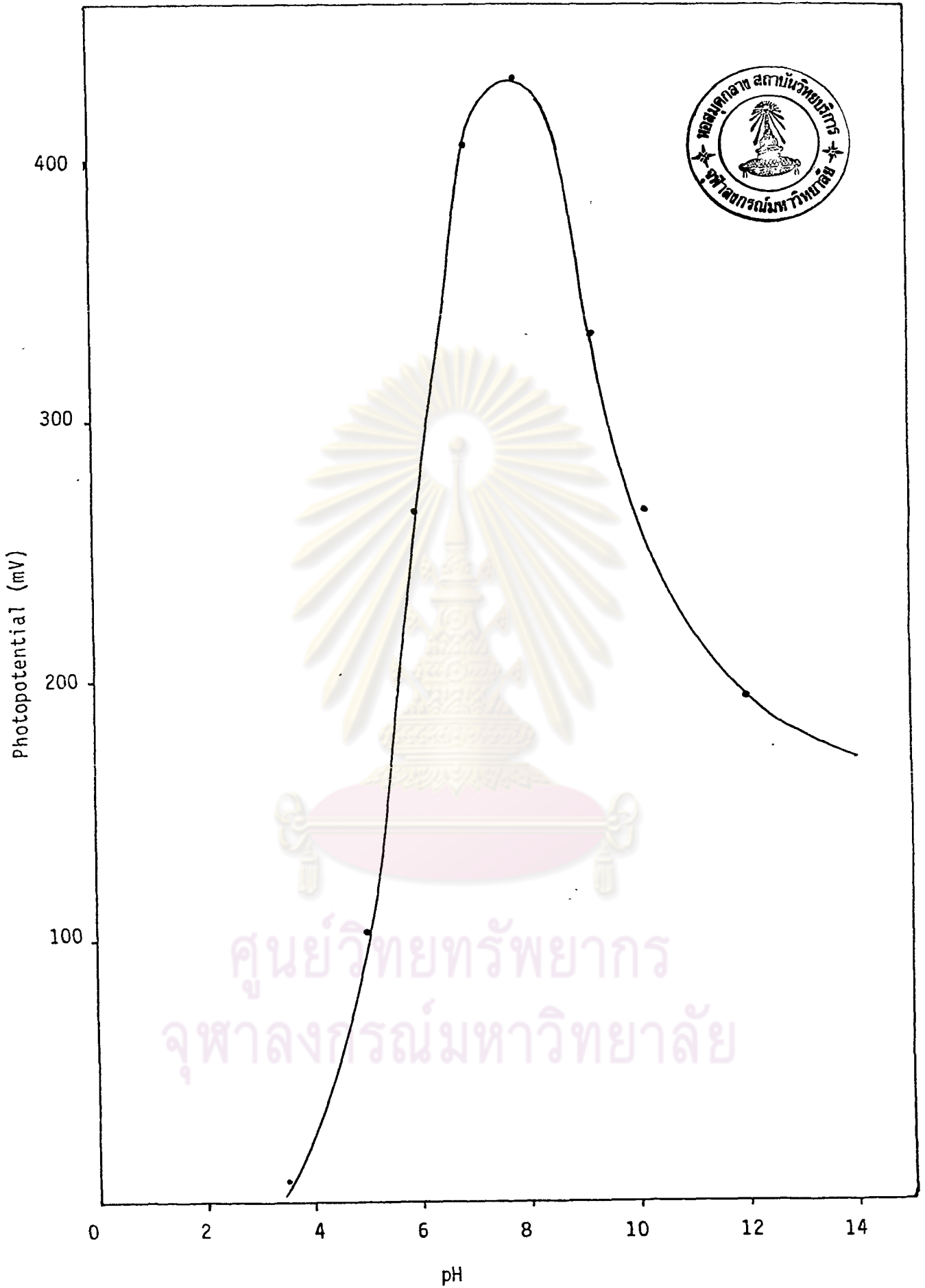


Figure 34. pH dependence on the photopotential of the Rb-Tea system : $[Rb] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[Tea] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$

The implicit conclusion that there is a competition between the photoreaction (between riboflavin and triethanolamine) and back-oxidation by oxygen is substantiated by the results shown in Figure 35 (b). If illumination is stopped during the passage of oxygen, the system exhibits a small additional increase in potential to another equilibrium value. Also, when oxygen is introduced in the dark after the first illumination cycle (Figure 35 (c)), further increases in potential are observed even with the light turned on. After oxygen has been removed in this last case, the potential behavior of the system under illumination is similar to that shown in the first case (Figure 35 (a)), i.e., only half of the maximum photopotential is recovered. In this respect, the Rb-Dea system shows a slightly 'better' performance.

Changes in photopotential with temperature are represented in Figure 36. Similar changes are recorded for the three cases: variation in the temperature of either compartment and of both compartments simultaneously. In general, the photopotential tends to decrease as the temperature goes up, suggesting a slight shift of equilibrium to the left and probably a corresponding negative enthalpy change for the forward reaction. Similar results have been obtained for the Rb-Dea system and the same interpretation applies in both cases.

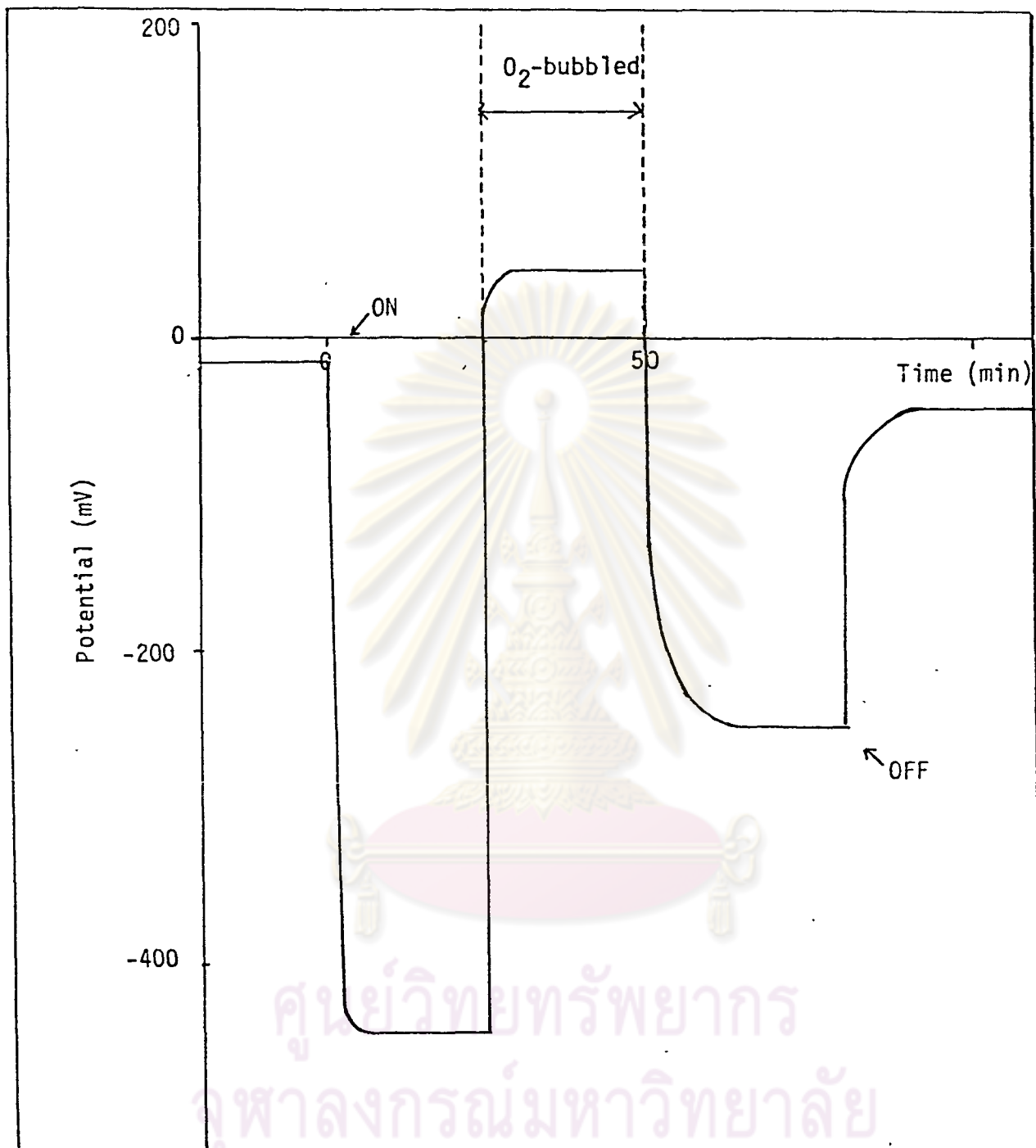


Figure 35. Effect of the oxygen gas on the photopotential of the Rb-Tea system : $[Rb] = 1.2 \times 10^{-4}$ mol dm⁻³ ; $[Tea] = 1.0 \times 10^{-3}$ mol dm⁻³ ; pH 7.90

(a) oxygen bubbled during photostationary state

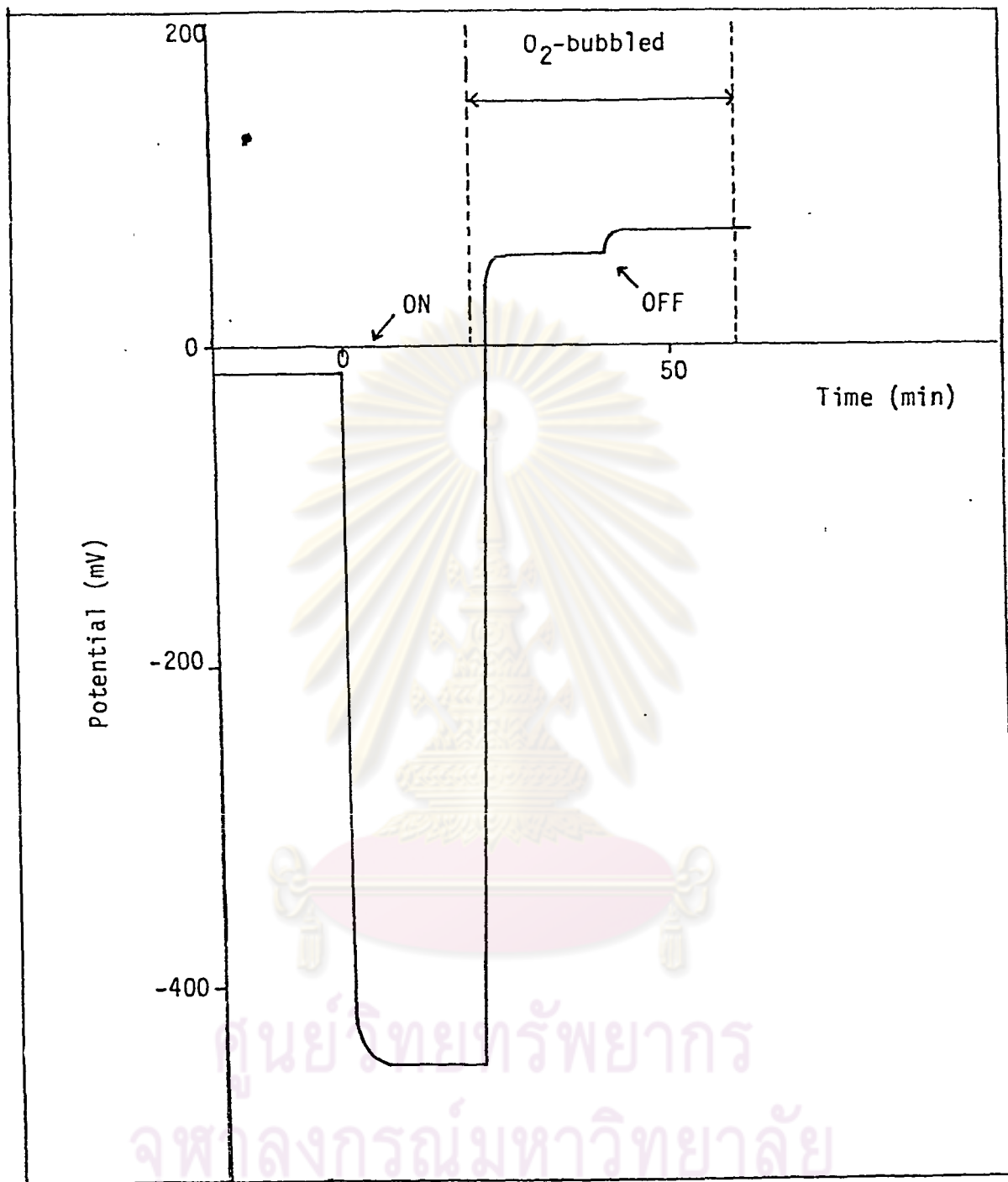


Figure 35. Effect of the oxygen gas on the photopotential of the Rb-Tea system : $[Rb] = 1.2 \times 10^{-4}$ mol dm^{-3} ; $[Tea] = 1.0 \times 10^{-2}$ mol dm^{-3} ; pH 7.90

(b) oxygen bubbled during and after illumination.

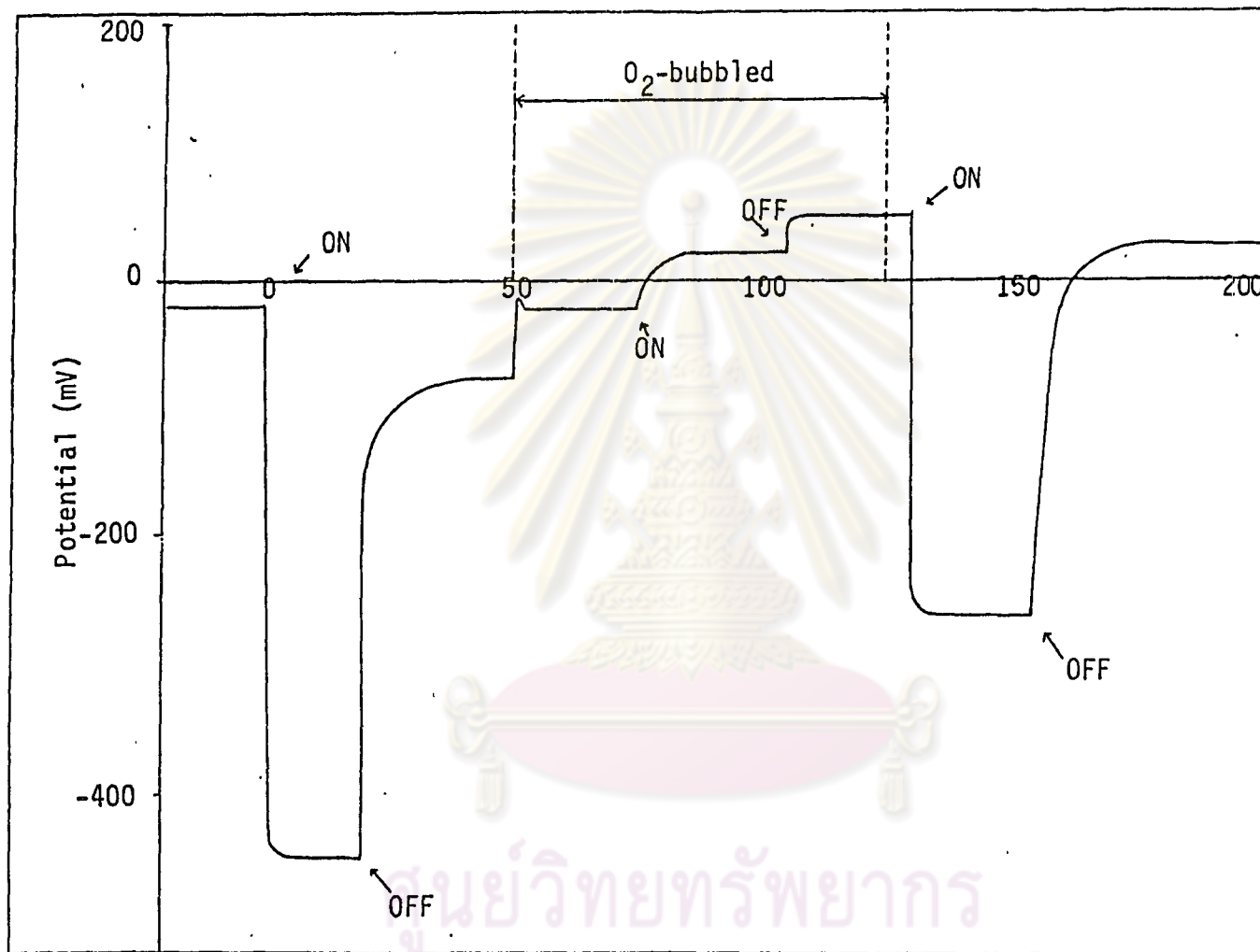


Figure 35. Effect of the oxygen gas on the photopotential of the Rb-Tea system : [Rb] = 1.2×10^{-4} mol dm⁻³ ; [Tea] = 1.0×10^{-2} mol dm⁻³ ; pH 7.90
 (c) oxygen bubbled after one illumination cycle.

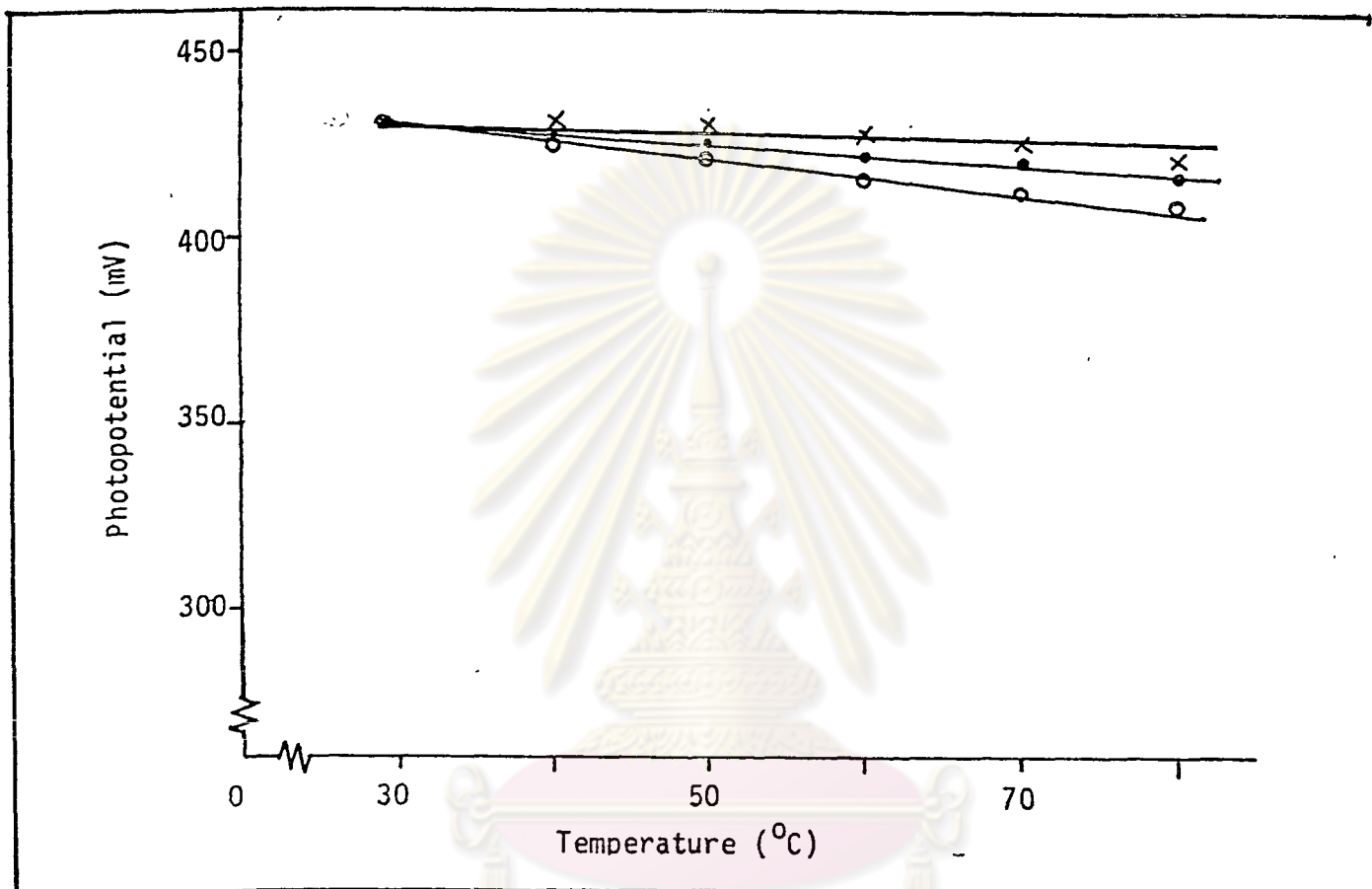


Figure 36. Variation of the photopotential of the Rb-Tea system with the temperature of the dark compartment (x), of the illuminated compartment (o), and of both compartments (•)
 $[Rb] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[Tea] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$; pH 7.90.

The effect of small amounts of organic solvents (methanol ethanol, isopropanol and tert-butanol) on the photopotential is more or less identical with that found for the Rb-Dea system. Since no definite conclusion can be drawn, further discussion will be omitted.



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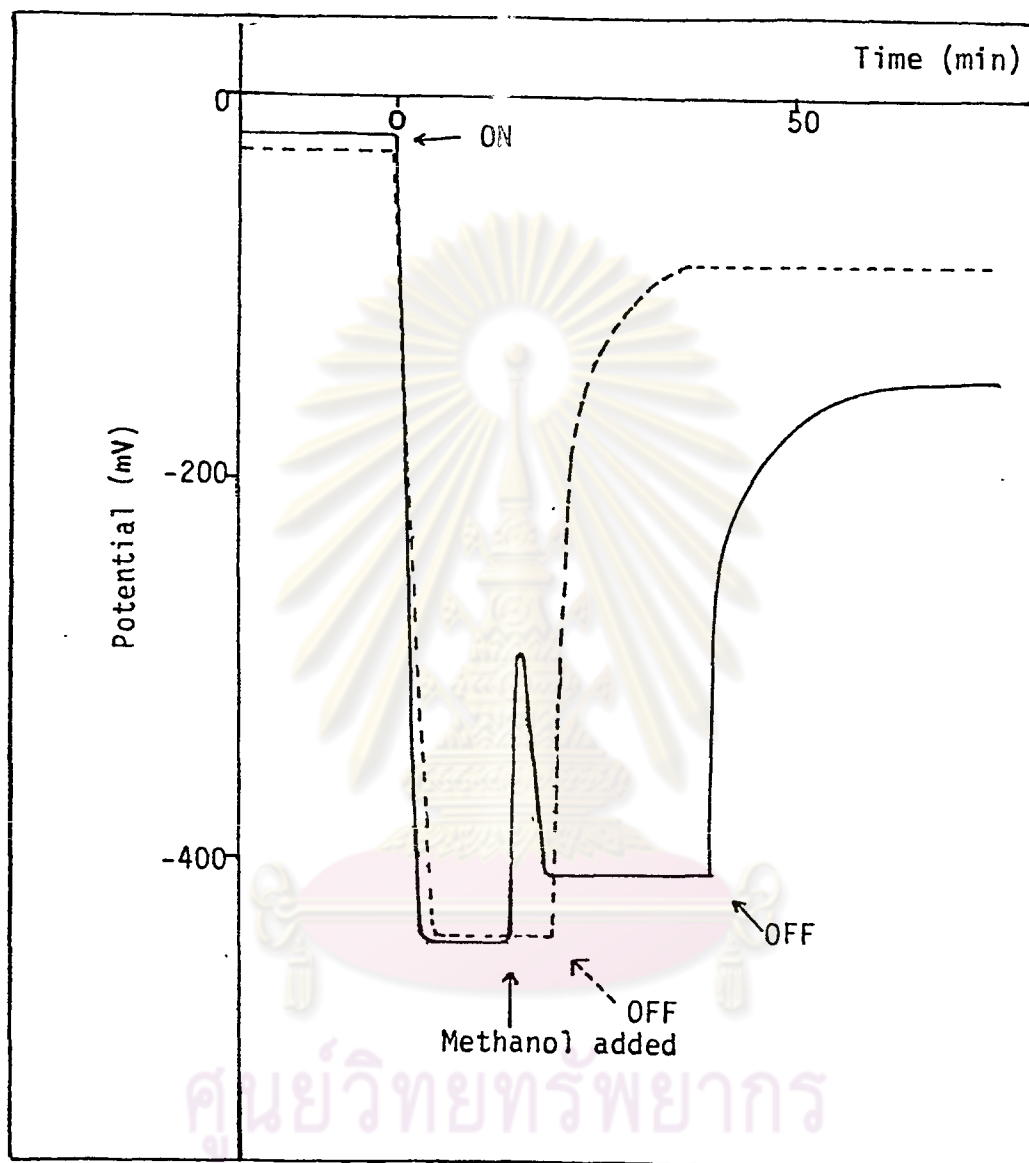


Figure 37. Effect of methanol (1.0 cm) on the photopotential of the Rb-Tea system : $[Rb] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[Tea] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$; pH 7.90.

- methanol added during photostationary state
 - - - - - methanol added in the dark

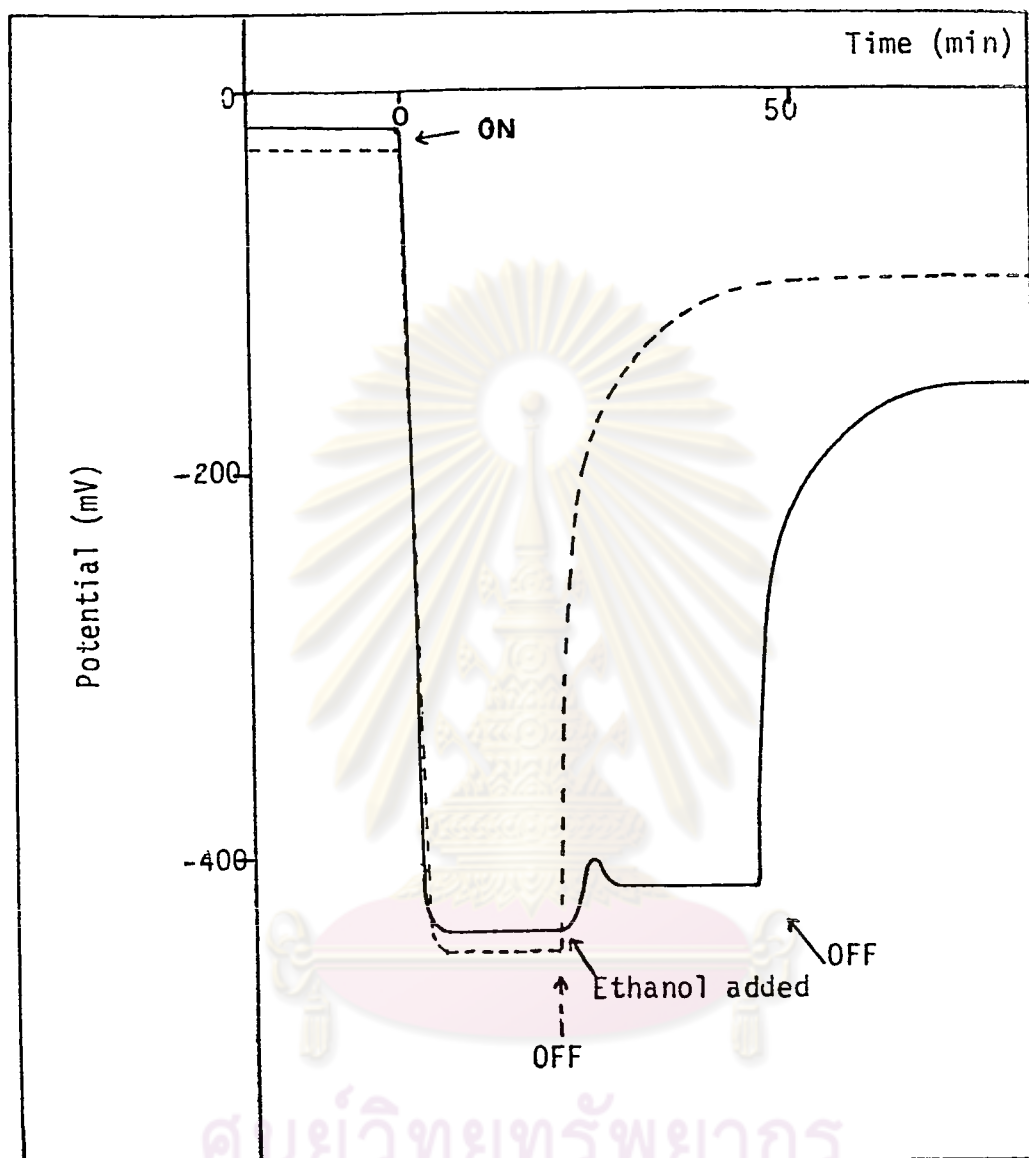


Figure 38. Effect of ethanol (1.0 cm³) on the photopotential of the Rb-Tea system : $[Rb] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[Tea] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$; pH 7.90.

— ethanol added during photostationary state
 - - - - ethanol added in the dark

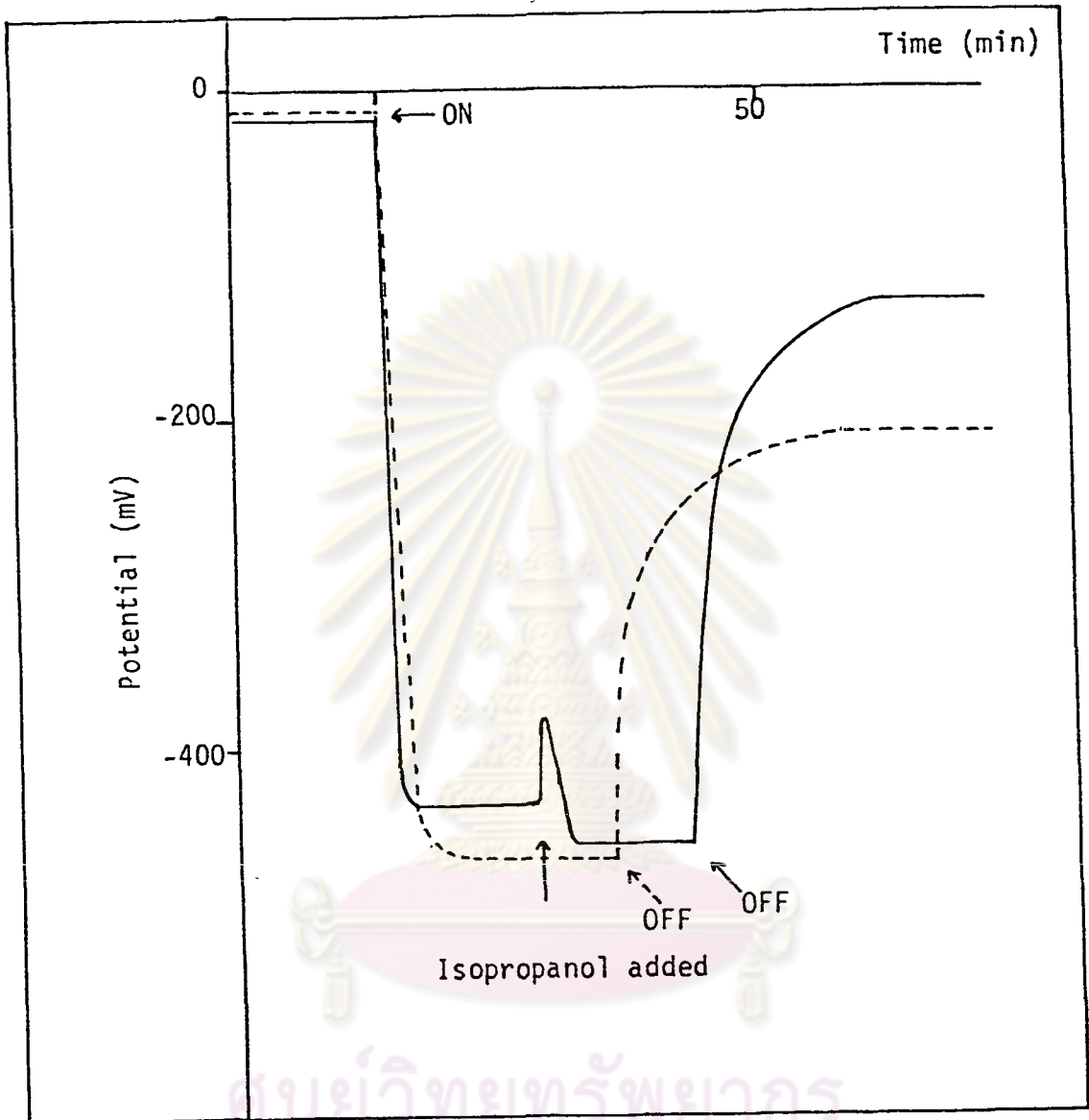


Figure 39. Effect of isopropanol (1.0 cm^3) on the photopotential of the Rb-Tea system : $[\text{Rb}] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{Tea}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$; pH 7.90.

- isopropanol added during photostationary state
- isopropanol added in the dark

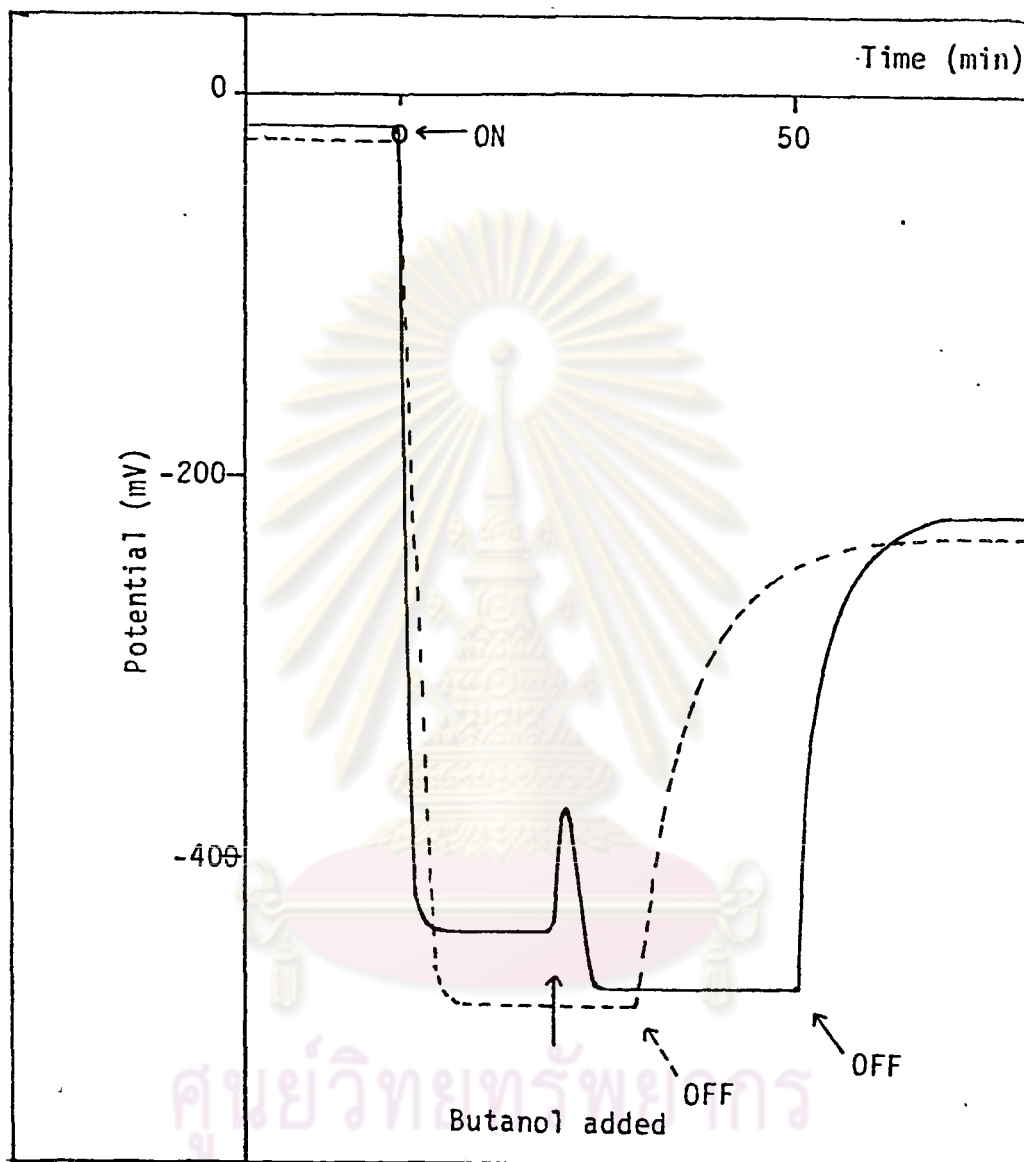


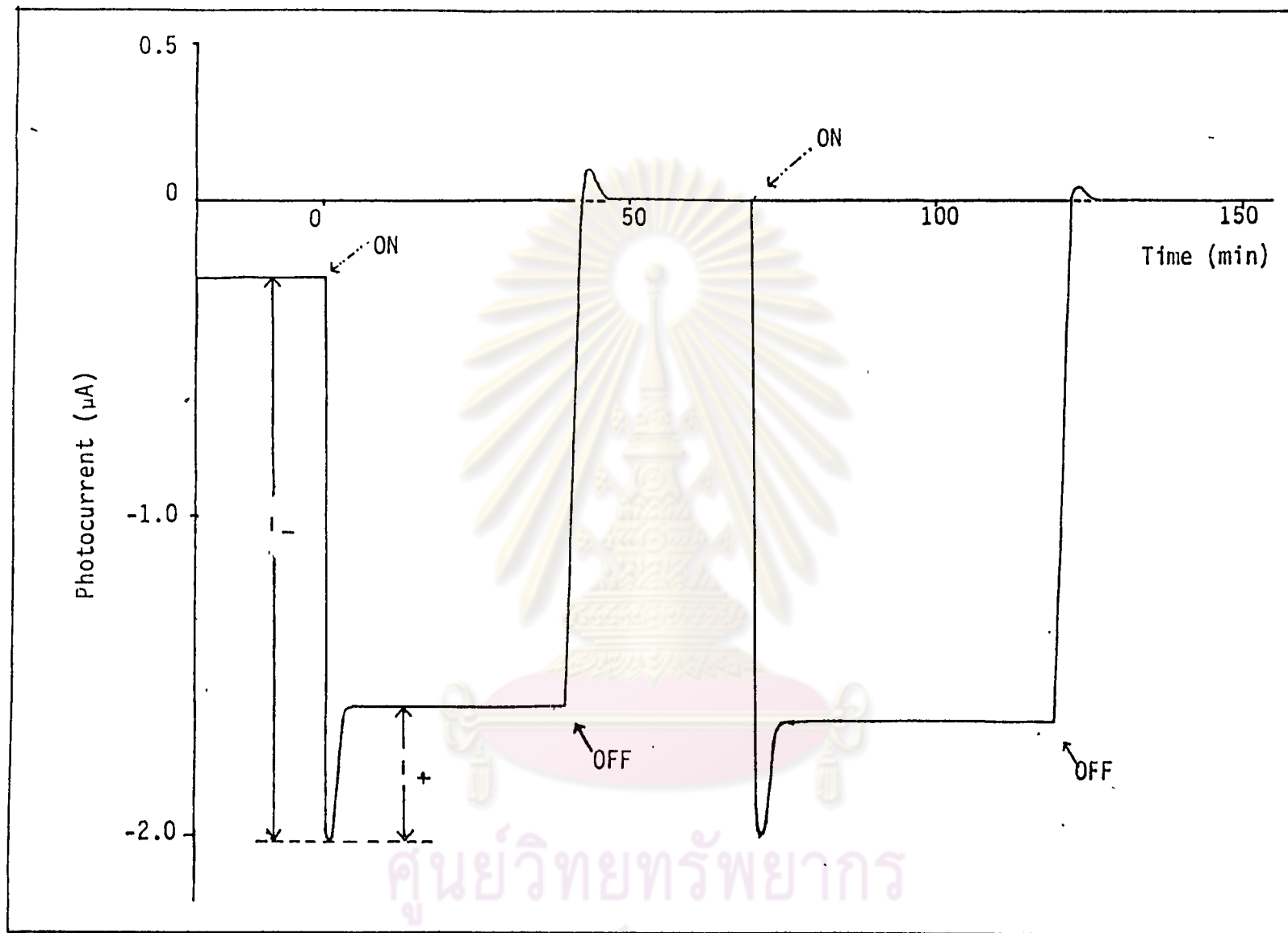
Figure 40. Effect of tert-butanol (1.0 cm³) on the photopotential of the Rb-Tea system : [Rb] = 1.2×10^{-4} mol dm⁻³ ; [Tea] = 1.0×10^{-3} mol dm⁻³ ; pH 7.90.

— tert-butanol added during photostationary state
 - - - - - tert-butanol added in the dark

4.3.2 Photocurrent study

The photocurrent-time curve, shown in Figure 41, is essentially the same as that obtained for the Rb-Dea system, although PC_{max} , PC_{eq} and i_{+} differ slightly for the two systems (Table 9). Discrepancies are, at least partly, due to difference in concentrations of diethanolamine and triethanolamine since photocurrent generation should be dependent on the concentrations of the species involved in the redox reaction.

The reaction scheme for this system is arrived at in much the same way as for the Rb-Dea system. Assuming that riboflavin is photoexcited and then reduced by triethanolamine in the illuminated compartment the main electrode-active species can be identified (14). Most probably the reduced form of riboflavin, RbH_2 , is responsible for electron transfer to the illuminated electrode. This process corresponds to the sharp, negative response giving rise to PC_{max} in Figure 41. Increasing the diffusion length has very little effect on PC_{max} and PC_{eq} , and thus on i_{+} and i_{-} (Figure 42). An appropriate explanation is that the active species at the dark electrode is one which is already present in the dark compartment at the very beginning of the reaction. The only likely choice in this case is riboflavin which is capable of extracting electron from the electrode. This latter electron transfer process corresponds to the



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Figure 41. Photocurrent behavior of the Rb-Tea system : $[Rb] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[Tea] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$; pH 7.90 ; diffusion length = 14.6 cm.

Table 9. Comparison of photocurrent between the Rb-Dea and the Rb-Tea system.

Photocurrent (μA)	Photogalvanic system	
	2 Rb-Dea	3 Rb-Tea
1 PC_{max}	-1.85	-2.03
$i_{-} = PC_{\text{max}} $	1.85	2.03
PC_{eq}	-0.87	-1.60
$i_{+} = PC_{\text{max}} - PC_{\text{eq}} $	0.98	0.43

1. the diffusion length = 14.6 cm.
2. $[Rb] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[Dea] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$; pH 8.43.
3. $[Rb] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[Tea] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$; pH = 7.90.

'positive' portion of the photocurrent response in Figure 41. A possible reaction scheme is, therefore, as shown in Figure 43.

Substantiating evidence for the above-proposed reaction scheme has been obtained from the study of the effect of oxygen on the photocurrent, the results of which are shown graphically in Figure 44 for the cases of oxygen bubbling in the dark compartment, in the

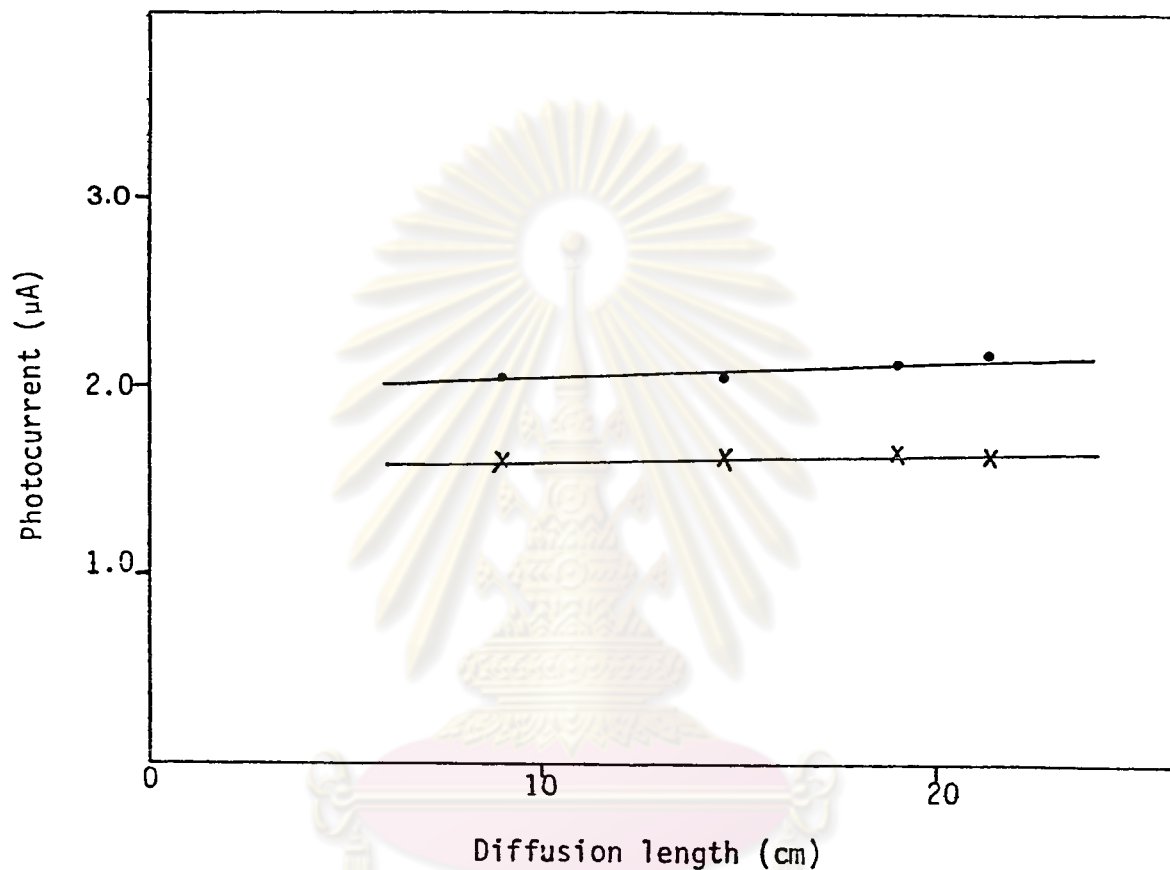


Figure 42. Effect of diffusion length between electrodes on PC_{max} and PC_{eq} : $[Rb] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[Tea] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$; pH 7.90 ; (o) PC_{max} ; (x) PC_{eq}

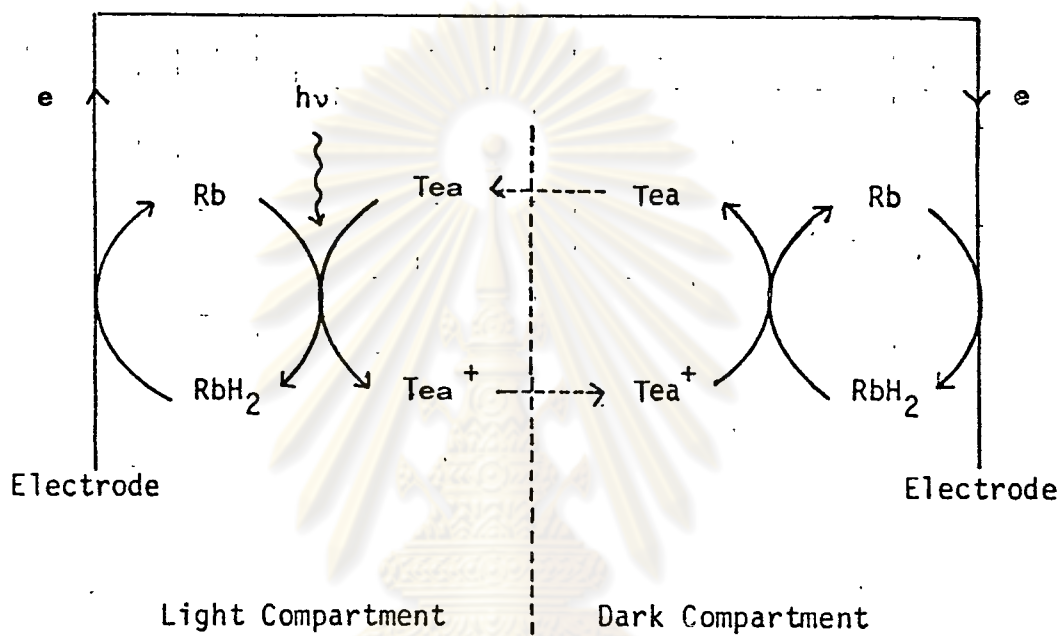


Figure 43. Reaction Scheme for photocurrent generation of Rb-Tea system.

illuminated compartment, and simultaneously in both compartments.

Bubbling oxygen through only the dark compartment should have a considerable effect on the electron transfer reaction at the dark electrode. Presumably, RbH_2 is reoxidized back to Rb at a rate greater than the normal rate of oxidation by Tea alone. Thus, i^+ show a large increase (Figure 44 (a) compared with Figure 41). In contrast, bubbling oxygen through the illuminated compartment produces a different effect—the photocurrent becomes anodic (positive). This alternation of sign implies that the illuminated electrode has now become a photocathode and the electron is now flowing through the external circuit to the electrode. The only possible explanation is that Rb^* in the illuminated compartment, apart from being reduced by Tea, can now extract electrons from the electrode and become reduced. Meanwhile, RbH_2 which can readily move to the dark electrode is capable of transferring electrons to the electrode and becoming Rb. Thus the direction of electron flow in the external circuit and the occurrence of the anodic current are accounted for. Similar results have been obtained for the Rb-Dea system but the effect is barely observable. Finally, with oxygen purging through both compartments (Figure 44 (c)), intermediate values of i^- and i^+ are obtained, suggesting counteractions of oxygen in the two compartments.

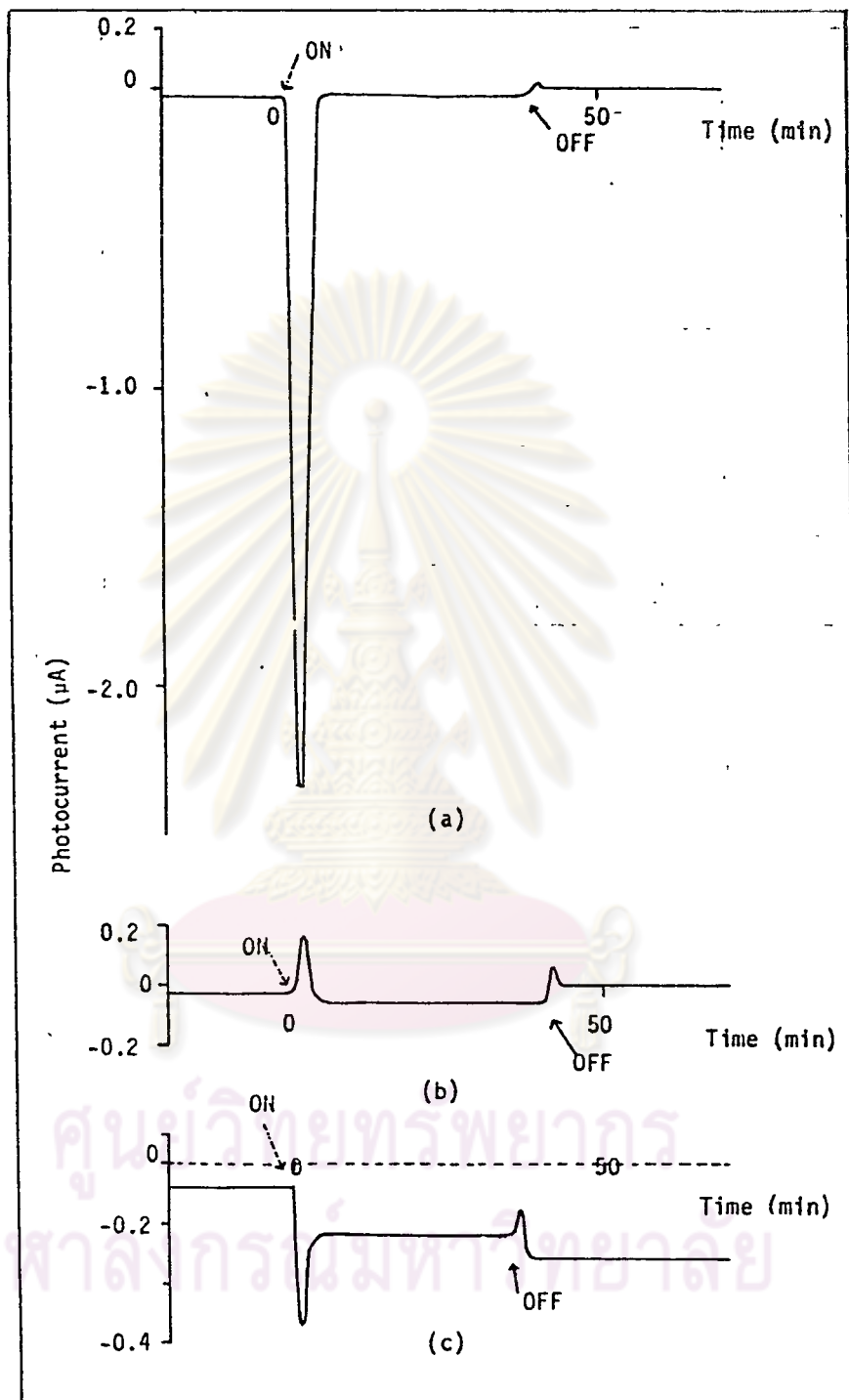


Figure 44. Effect of oxygen gas on the photocurrent of the Rb-Tea system: $[\text{Rb}] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{Tea}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$; pH 7.90

(a) oxygen bubbled through the dark compartment

(b) oxygen bubbled through the illuminated compartment

The variations of PC_{\max} , PC_{eq} and i_{\max}^+ with temperature are tabulated in Tables 10, 11 and 12. Taking $i_{\max}^- = |PC_{\max}^-|$ and $i_{\max}^+ = |PC_{\max}^+ - PC_{eq}^+|$ as before, it is clearly seen that i_{\max}^- and i_{\max}^+ increase with temperature (Figures 45 and 46). These increases are more pronounced when the temperature of the illuminated compartment is raised, whether or not the temperature of the other half-cell is raised. Since the temperature range involved is relatively low, it can be safely assumed that none of the dissolved substances undergo thermal decomposition. Elevation of temperature then leads only to increased mobility for all species and, inevitably, to ohmic loss. Again, in this case the effect on mobility, leading to large i_{\max}^- and i_{\max}^+ , outweighs the effect on ohmic loss.

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Table 10. Effect of the temperature of the dark compartment on the photocurrent of the Rb-Tea system.*

Temperature							
(μ A)	($^{\circ}$ C)	29	40	50	60	70	80

$i = \left \begin{matrix} \text{PC} \\ - \\ \text{max} \end{matrix} \right $		2.25	2.63	2.60	3.35	3.70	3.82
PC		-1.70	-1.60	-0.90	-1.05	-1.05	-0.95
$i = \left \begin{matrix} \text{PC} & -\text{PC} \\ + & \text{max} & \text{eq} \end{matrix} \right $		0.55	1.03	1.70	2.30	2.65	2.87

Table 11. Effect of the temperature of the illuminated compartment on the photocurrent of the Rb-Tea system.*

Temperature						
(μ A)	($^{\circ}$ C)	29	40	50	60	70

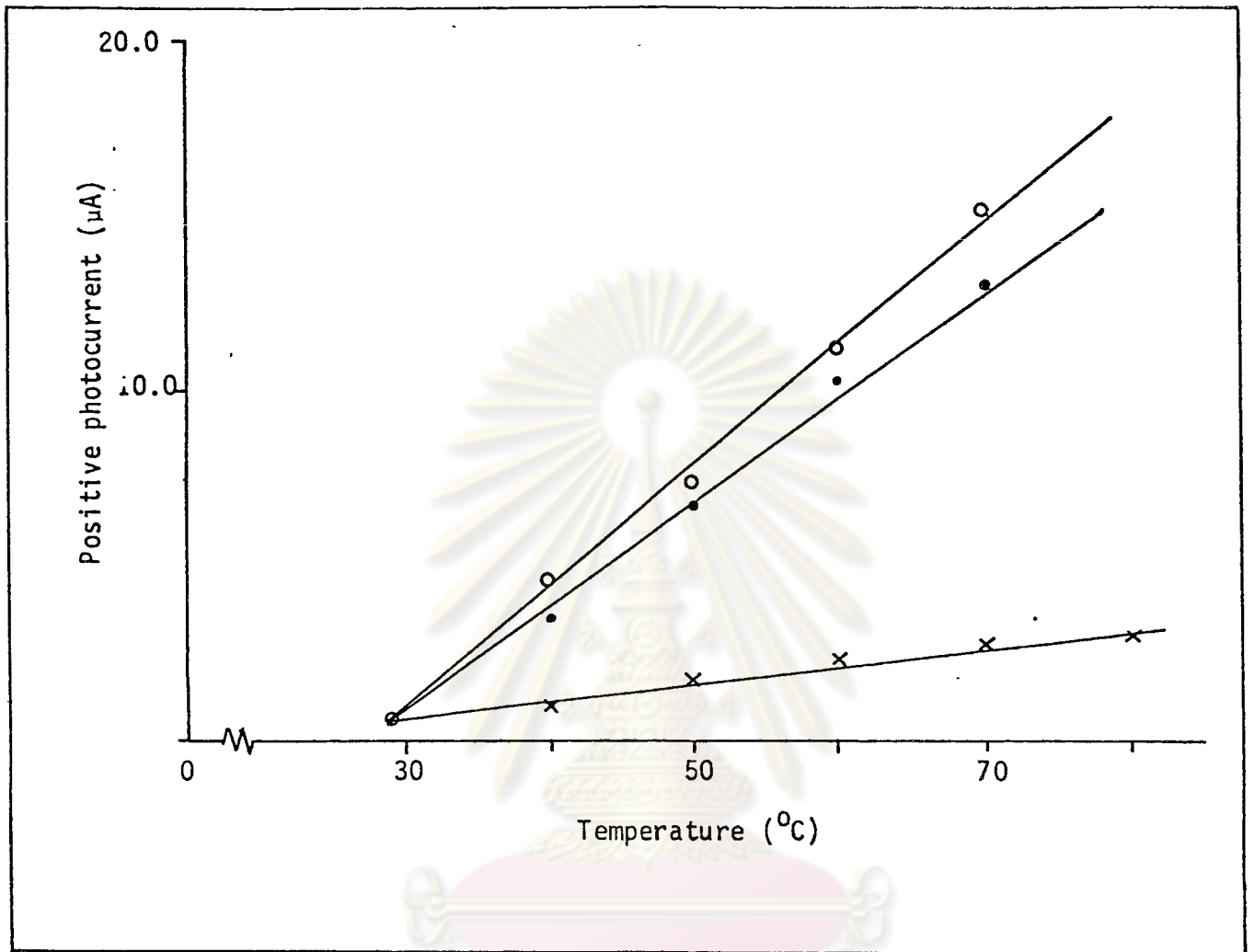
$i = \left \begin{matrix} \text{PC} \\ - \\ \text{max} \end{matrix} \right $		2.25	6.50	9.25	13.0	16.9
PC		-1.70	-1.88	-1.90	-1.80	-1.75
$i = \left \begin{matrix} \text{PC} & -\text{PC} \\ + & \text{max} & \text{eq} \end{matrix} \right $		0.55	4.62	7.35	11.2	15.15

Table 12. Effect of the temperature of both compartments on the photocurrent of the Rb-Tea system.*

temperature						
(μ A)	($^{\circ}$ C)	29	40	50	60	70

$i = \left \begin{matrix} \text{PC} \\ - \\ \text{max} \end{matrix} \right $		2.25	5.20	8.43	12.15	14.85
PC		-1.70	-1.75	-1.68	-1.90	-1.90
$i = \left \begin{matrix} \text{PC} & -\text{PC} \\ + & \text{max} & \text{eq} \end{matrix} \right $		0.55	3.45	6.75	10.25	12.95

* [Rb] = 1.2×10^{-4} mol dm⁻³ ; [Tea] = 1.0×10^{-2} mol dm⁻³ ; pH 7.90; diffusion length = 21.3 cm.



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Figure 45. Variation of the positive component of the photocurrent (i) with the temperature of the dark compartment (x), of the illuminated compartment (o), and of both compartments (o)
 $[Rb] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[Tea] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$; pH 7.90

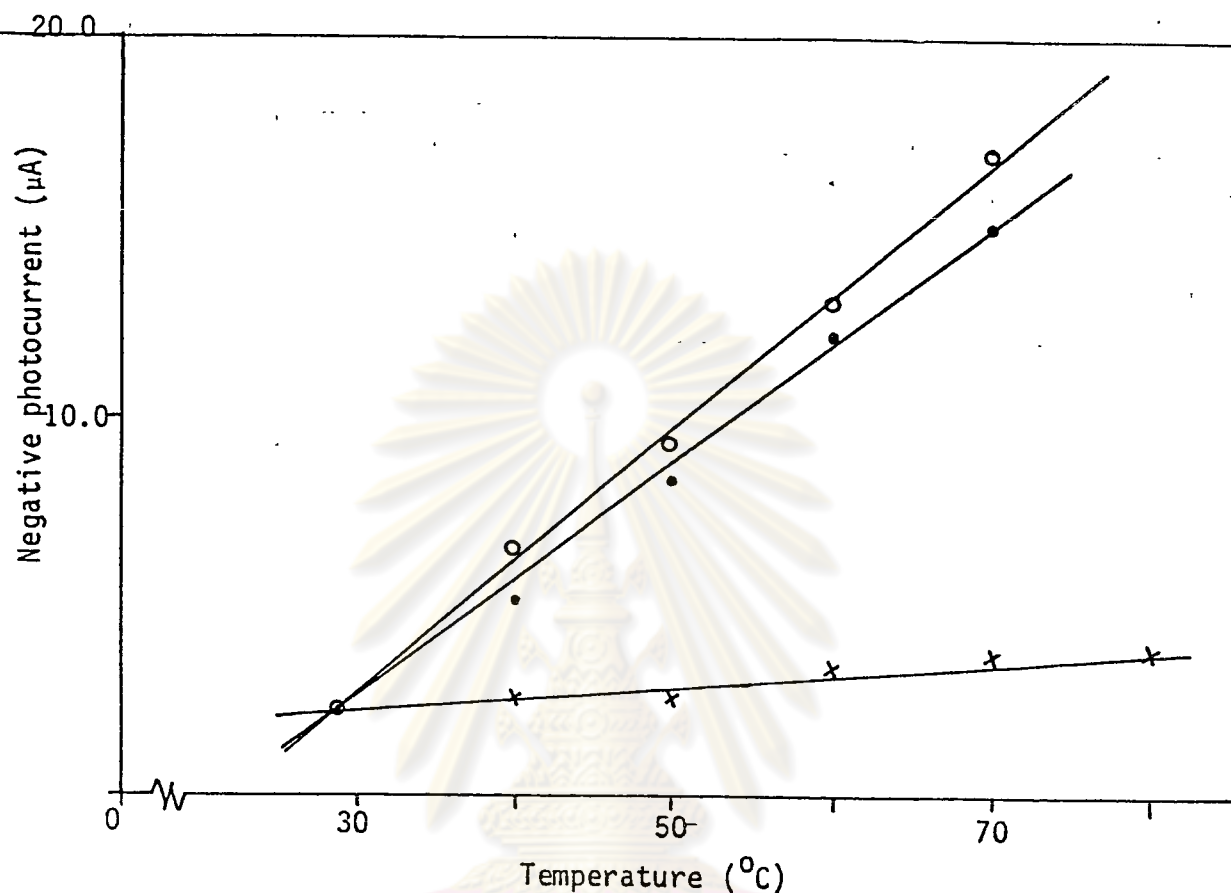


Figure 46. Variation of the negative component of the photocurrent (i) with the temperature of the dark compartment (x), of the illuminated compartment (o), and of both compartments (o)
 : $[Rb] = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$; $[Tea] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$; pH 7.90

4.4 Cell Efficiencies

The efficiency of each of the two photogalvanic systems were calculated by taking the efficiency as the ratio of the power output of the cell to the radiant energy absorbed. Assuming each cell operating at its photostationary state, the power output was readily calculated in milliwatts per unit area of electrode. Results are shown in Table 13. The efficiencies are, respectively, 0.011 and 0.016% for the Rb-Dea and Rb-Tea systems. These values are lower than those for the iron-thionine system (0.03%) and the EDTA-methylene blue system (0.04%) but are in the same order of magnitude.



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Table 13. Cell Efficiencies (light intensity = 6.7 mW/cm^2 ; electrode area = 0.64 cm^2)

System	PV (V)	photocurrent (A)	Power Output (mW/cm^2)	Cell Efficiency (%)
Rb-Dea	0.520	0.9×10^{-6}	0.73×10^{-3}	0.011
Rb-Tea	0.430	1.6×10^{-6}	1.07×10^{-3}	0.016



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