Enhanced Electrochemifluorescence and Reduction Mechanism of Acetoxy Coumarin Derivatives in Acetonitrile Solution

Sung Hyun Kim, Eun Joo Jung, Eun Mi So, Chang Zhe Shen, Hyun Ja Chun, Young Man Kim,† and Il Kwang Kim*

*Department of Bio-nano Chemistry, College of Natural Science and Institute of Basic Natural Science, Wonkwang University, Iksan 570-749, Korea. *E-mail: ilkim@wonkwang.ac.kr*
†Advanced Analysis Center, Korea Institute of Science and Technology, Seoul 136-791, Korea
Received November 14, 2005

The electrochemical reduction of coumarin, 7-acetoxy-4-methyl coumarin (AMC), and 7-acetoxy-4-bromomethyl coumarin (ABMC), in 0.1 M tetraethyl ammonium perchlorate/acetonitrile solution was carried out by direct current, differential pulse polarography, cyclic voltammetry, and controlled potential coulometry. The electrochemical reduction of ABMC was proceeded through three steps of electron transfer coupled with the chemical reactions. The color of solution was changed to yellow when the carbonyl group was reduced during 2nd step (−1.8 volts) and independented with cleavage of bromo group. Highest fluorescence intensity showed when the electrochemical reduction of AMC was controlled at near the potential (−2.3 volts *vs.* Ag/AgCl).

Key Words : Coumarin derivatives, Differential pulse polarography, Cyclic voltammetry, Fluorescence, Electrochemifluorescence

Introduction

Coumarin is widely used as a raw material of blood anticoregulator,[1,2] rodenticide,[3] perticide,[4,5] and aromatic essence additive,[6] *etc*., since it has been firstly extracted from tonka bean. Recently, coumarin derivatives are well-known fluorescence dyes for their high photoluminescence (PL) quantum efficiencies, and applied to electro-optic materials.[7-9]

Nemkovich[10] reported the results from electro-optic absorption and emission measurements on the equilibrated ground state and the excited Frank-Condon state of four highly efficient coumarin laser dyes. Sentein[11] studied the influence of the doping ratio on current-voltage characteristics and electroluminescence quantum efficiency of single-layer coumarin doped polymer for blue light-emitting diodes.

Justin Tomas[12] described the preparation of a coumarin series with peripheral arylamines which are green or blue emitting and capable of hole transporting. Chen[13] discovered two stericly hinered green coumarin derivatives which showed significantly thermal stability and overall electrochemical luminescence[14] performance.

Novel coumarin terminated with poly(*p*-phenylene) vinylenes were synthesized and the resulting coumarin end-capped polymer film gave yellow photoluminescence with a maximum intensity at 560 nm.[15] Coumarin modified mesoporous silica expected to open up further application possibilities which can photocontrolled reversible release of guest molecules and drug delivery.[16] It was employed as a dye sensitizer[17] in dyesensitized solar cells and showed efficient photo-to-electron conversion properties.

On the other hand, electrochemical reduction of coumarin have started to study by Harle[18] and Capka.[19] Zuman[20-22] have reported a half-wave potential and substituents effect for coumarin derivatives and Gourley[23] have obtained the result that coumarin derivative becomes dihydrocoumarins by the electrochemical reduction in the presence of tertiary amine coumarin. Reddy[24] have suggested a polarographic reaction mechanism of 3-acetyl coumarin and Partridge,[25] Bond[26] have explained a phenomenon that coumarin becomes adsorbed to mercury electrode. Helin[27] have reported the electrochemiluminescence of 4-methyl coumarin derivatives induced by hot electrons into aqueous electrolyte solution. Diez[28] have surveyed the voltammetric determination of coumarin in the emulsified media and Wang[29] have done a differential pulse voltammetric determination with 7-hydroxy coumarin of human urine. Wang[30] have made an amperometric biosensor by modifying antibody of 7-hydroxy coumarin with glassy carbon electrode, and have investigated antibody specificity and antibody-antigen interaction kinetic. 7-hydroxy coumarins were studied using cyclic voltammetry, differential pulse voltammetry, and chronocoulometry. The results showed that the coumarins undergo a pH-dependent, irreversible oxidation with product adsorption.[31]

In this study, we have performed that the electrochemical reduction and electrogenerated chemifluorescence of 7-acetoxy-4-bromomethyl-coumarin (ABMC), 7-acetoxymethyl-coumarin(AMC), and coumarin as showed the structure in Figure 1 by polarography, cyclic voltammetry (CV), and controlled potential electrolysis (CPE).

Experimental Section

Reagents. Coumarin derivatives (Aldrich Co.), tetraethyl-ammonium perchlorate (TEAP) and tetraethylammonium hydroxide (TEAOH) were used as purchased. Acetonitrile (AN) was purified by Walter and Ramalay method.[32]

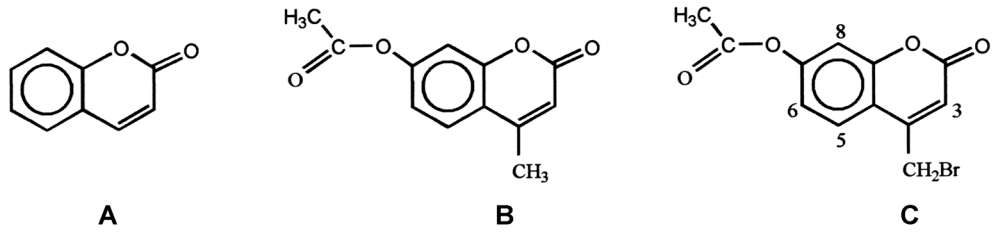


Figure 1. Structure of A: coumarin, B: 7-acetoxy-4-methyl-coumarin (AMC), C: 7-acetoxy-4-bromomethyl-coumarin (ABMC).

Nitrogen gas was passed through basic pyrogallol solution first and calcium chloride layer, and acetonitrile last.

Instruments. By connecting PARC model 303A Static Mercury Drop Electrode System (3 electrode system for ohmic drop compensation) and PARC model RE0074 X-Y Recorder with EG & PARC model 174A Polarographic Analyzer. Cyclic voltammogram was obtained by PARC model 175 Universal Programmer and PARC model 173 Potentiostat was used to perform controlled potential electrolysis. Fluorescence emission from electrochemically generated coumarin was recorded on a Jasco spectrofluorometer equipped with a spectra correction unit and quartz cells. Measurement of pH was performed with Model 520A Digital pH-metal from Orion Research Co., and Thermo Cool (A-Line Lab.) was used for temperature control.

Procedure. The electrochemical cell was constructed with Ag/AgCl reference electrode, platinium wire auxillary electrode and static mercury drop working electrode (drop size: medium). Polarograms were obtained under nitrogen gas passed through 0.1 M TEAP-AN solution for 8 min. and also proceeded with changing pH and temperature. Potentiostat was controlled at constant potential with electrometer probe to proceed stepwise reduction. The fluorescence spectra were obtained by exciting at a λmax that known with uv/vis absorption spectra of the products.

Results and Discussion

Diffusion current of coumarin derivatives. The typical direct current (DC) and the differential pulse polarograms (DPP) of coumarin, AMC and ABMC in 0.1 M TEAP-AN solution were obtained. The polarograms and cyclic voltammograms are shown in Figure 2, and Figure 3, respectively. We were able to interpret that step 1 was bromide reduction of ABMC and step 2 was reductive hydrogenation[17,22] of coumarin ring carbonyl group and step 3 was cleavage of ABMC acetoxy group or dihydrogenation of coumarin ring double bond and dimerization in Figure 2 and Figure 3. In order to know whether each reduction wave is caused by a diffusion wave or by a chemical reaction, it is firstly investigated the changes of the limiting current according to increases in concentration. The reduction waves were proportionated to concentration indicating that the currents was caused by diffusion.

As the second proof of diffusion current,[33] DC polarogram was obtained and calculated the percentage of $\Delta i/\Delta T$ by changing the temperature condition of a sample solution at intervals of 5 °C from 10 °C to 35 °C. From the result that $\Delta i/\Delta T$ percentage for reduction stage 1, 2 and 3 are 1.09, 1.26 and 1.05% respectively, we could assure that each reduction current is diffusion current. The diffusion current[33] is proportionate to $m^{2/3}t^{1/6}$ according to Ilkovic equation. DC and DP polarograms were obtained by changing drop's life

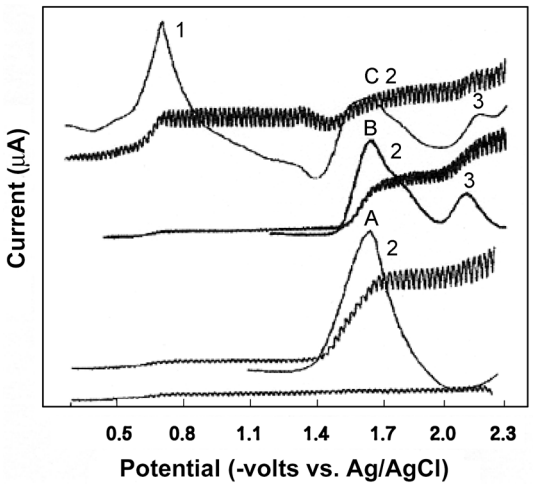


Figure 2. Typical DC and DP polarograms of coumarin derivatives in 0.1 M TEAP-AN solution. Scan rate: 50 mV/sec. Current range: 0.02 mA. A: 1×10^{-3} M coumarin, B: 1×10^{-3} M AMC, C: 5×10^{-4} M ABMC.

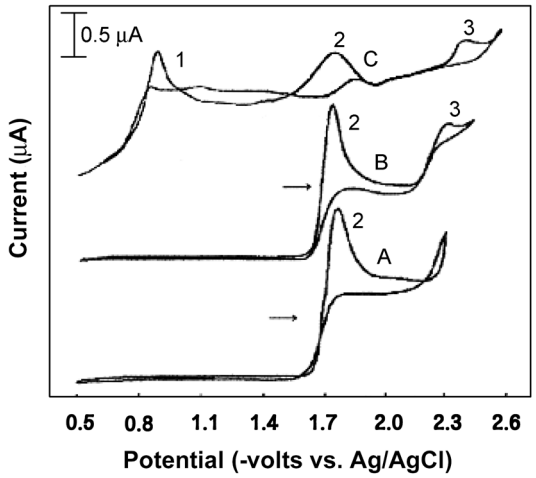


Figure 3. Typical cyclic voltammograms of coumarin derivatives in 0.1 M TEAP-AN solution. Scan rate: 50 mV/sec. A: 1×10^{-3} M coumarin, B: 1×10^{-3} M AMC, C: 5×10^{-4} M ABMC.

time of mercury into 0.5, 1, 2 and 5 sec, and weighed the dropped mercury drops per life time for a fixed time in a blank solution. Reduction current values acquired from each reduction step 1, 2 and 3 have showed a good proportion to $m^{2/3}t^{1/6}$ values of mercury drop. From the result of cyclic voltammogram as shown in Table 2, $i_{pc}/\sqrt{v}$ values were nearly constant for the different scan rate. These various results showed that each reduction step of ABMC is diffusion controlled ones.

Irreversibility of Electrochemical Reduction of Coumarin Derivatives. The results of plotting $\log[i/(i_d - i)]$ values of the reduction steps for the changes in potentials are shown in Figure 4. The slope and electron transfer number obtained from the slope of Figure 4 were noted in Table 1, with electron number obtained by controlled potential coulometry. The changes of $i_{pc}/\sqrt{v}$ value for scan rate obtained from cyclic voltammogram (Fig. 3) were shown in Table 2.

On the plot of $\log[i/(i_d - i)]$ *vs.* potentials for polarograms, if the slope value is 59.1/n mV or the potential difference value of $E_{3/4}$-$E_{1/4}$ comes to 56.4/n mV, the electrode reaction is close to reversibility.[33] An irreversible process can defined as the peak potential difference between E_{pc} and E_{pa} becomes larger the above criteria. For a totally irreversible wave, ip is also proportional to C_o^* and $\sqrt{v}$, but E_p is a function of scan rate, shifting to a negative potential direction by an amount $30/\alpha$na mV for each tenfold increase in scan rate at 25 °C. In Table 1, when the solpe of the 1st reduction wave is 84 mV and $E_{3/4} - E_{1/4}$ value is 82 mV, and the slope of the 2nd reduction wave is 73 mV and $E_{3/4} - E_{1/4}$ value is 72 mV, it means that the 1st and 2nd reduction waves were proceeded to the irreversible process. And, from the result of cyclic voltammogram in Table 2, the peak potential has moved to negative potential over $30/\alpha$na mV as scan rate increased, which is interpreted as an irreversible process. For the all of the three reduction waves, each anodic peak current for cathodic peak currents did not appear in CV.

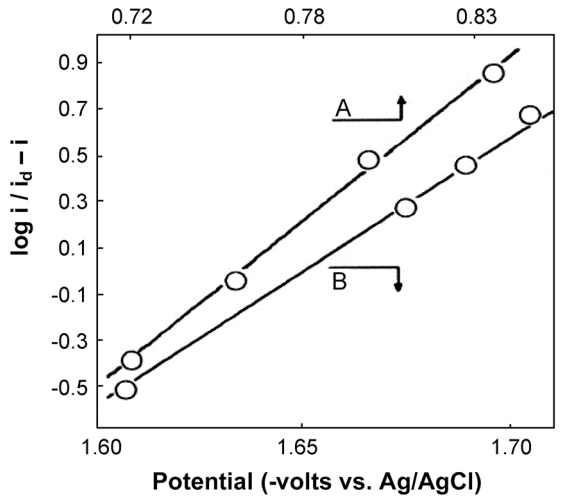


Figure 4. A plot of log $i/i_d - i$ *vs.* potential for polarograms on the 1 $\times 10^{-3}$ M ABMC. A: 1st wave: slope 84 mV, B: 2nd wave: slope 73 mV, *: 3rd wave: poor DC polarogram to plot.

Table 1. Polarographic data on the reduction of 1×10^{-3} M ABMC in 0.1 M TEAP-AN solution. Scan rate: 50 mv/sec. Current range: 0.02 mA

Reduction step	$-E_{1/2}$ (volts)	slope (mV)	$E_{3/4}-E_{1/4}$ (mV)	αn (polarography)	n (coulomety)
1st	0.58	84	82	0.70	1.70(≅ 2.0)
2nd	1.65	73	72	0.81	2.20(≅ 2.0)
3rd	2.25	poor to	define	–	0.78(≅ 1.0)

Table 2. Cyclic voltammetry data for the reduction of 1×10^{-3} M ABMC in 0.1 M TEAP-AN solution. Scan rate: 50 mv/sec. Current range: 0.02 mA

Reduction step	Scan rate (mV/sec)	Peak potential (volts)		Current (μA)		$i_{pc}/v^{1/2}$
		$-E_{pc}$	$-E_{pa}$	i_{pc}	i_{pa}	
1st	200	0.94	–	1.75	–	0.53
	100	0.85	–	1.68	–	0.57
	50	0.85	–	1.20	–	0.57
2nd	200	1.83	–	1.15	–	0.08
	100	1.72	–	0.97	–	0.09
	50	1.72	–	0.60	–	0.08
3rd	200	2.37	–	1.15	–	0.06
	100	2.31	–	0.97	–	0.06
	50	2.31	–	0.60	–	0.06

Therefore, it means that all the three reduction steps were an irreversible processes.

Effect of pH. By considering of diffusion current and halfwave potentials of polarogram for the changes of pH, a reaction process can be easily defined. pH of sample solution changed with TEAOH and $HClO_4$ from pH 2 to pH 11. The changes of wave peak potential according to pH were appeared in Figure 5. The peaks potential and current have been almost constantly maintained without a noticeable

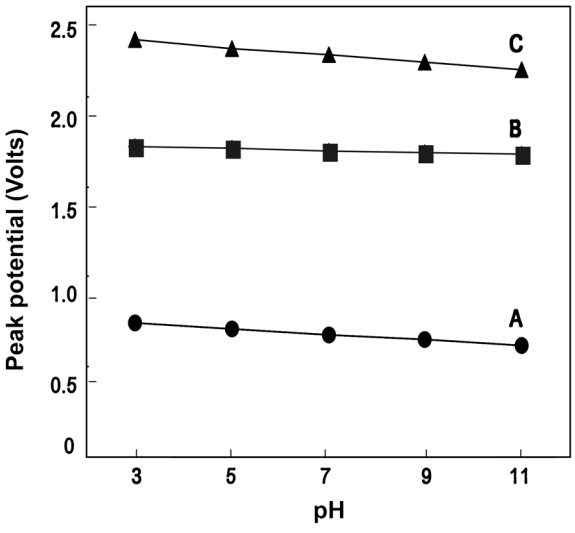
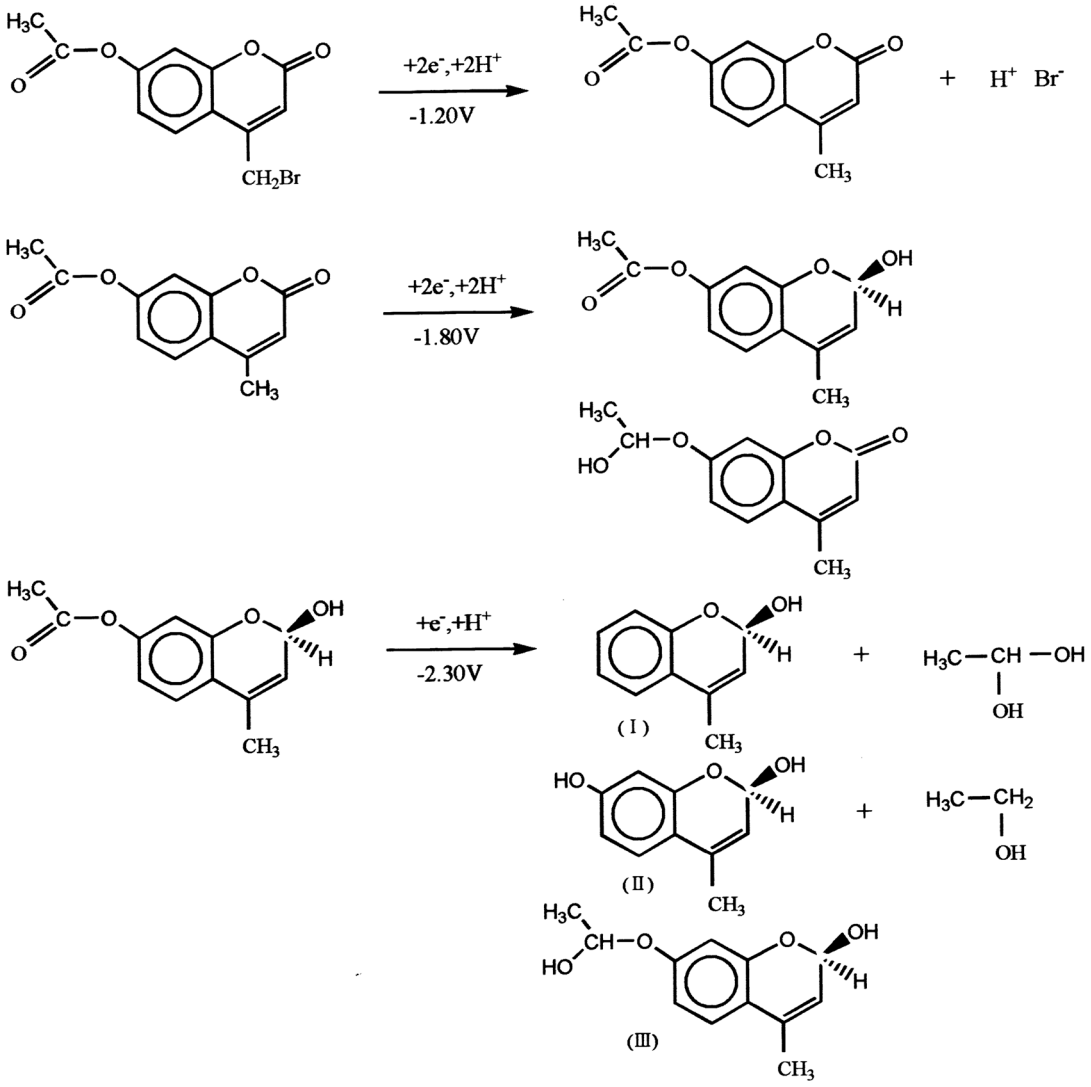


Figure 5. Effect of pH change in peak potentials of 1×10^{-3} M ABMC in 0.1 M TEAP-AN solution. ● : 1st wave ■ : 2nd wave ▲ : 3rd wave.



Scheme 1. The proposed electrochemical reduction mechanism on the ABMC.

change between pH 2 and pH 11. This means that it is not affected on the electron transfer by adding TEAOH or $HClO_4$ and the whole electrode reaction is EC mechanism as proceeding with electron transfer before chemical reaction. The proposed electrochemical reduction mechanism of ABMC was showed at Scheme 1.

Controlled Potential Electrolysis (CPE). From cyclic voltammetry of ABMC shown in Figure 3, −1.2 volts was selected for the 1st, −1.8 volts for the 2nd and −2.3 volts for the 3rd electrolysis and controlled potential electrolyzed on mercury pool working electrode with stirring. Higher negative potential than the peak potentials obtained from cyclic voltammetry in Figure 3 were fixed to perform the controlled potential electrolysis satisfactorily.

After the 1st electrolysis at −1.2 volts, the solution was changed to yellow color, but the yellow color was turned to colorless after a white precipitate of AgBr was formed by dropping $AgNO_3$ solution. This is strong evidence that the bromo group was reduced and removed from ABMC at −1.2 volts. After the 2nd electrolysis at −1.8 volts, the reduction

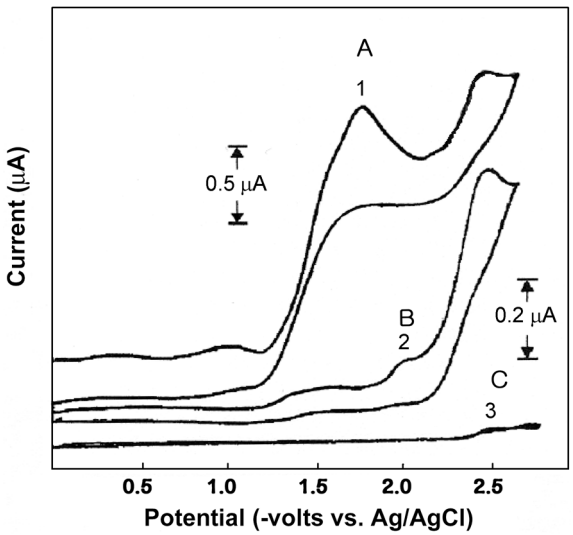


Figure 6. Cyclic voltammograms of electrolyzed solution for ABMC. A: after 1st step electrolysis at −1.2 volts, B: after 2nd step electrolysis at −1.8 volts, C: after 3rd electrolysis at −2.3 volts.

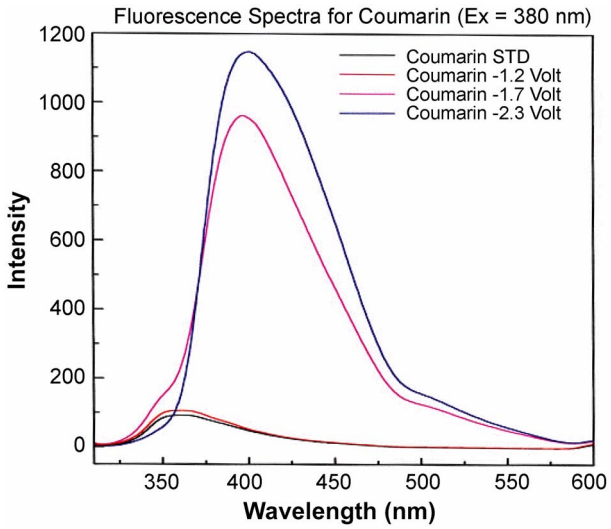


Figure 7. Fluorescence spectra for the coumarin basic molecule depend on the controlled potential of electrolysis.

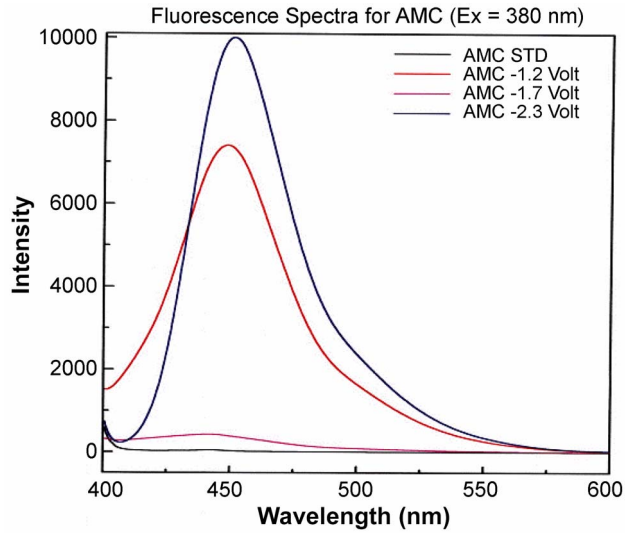


Figure 8. Fluorescence spectra for the AMC depend on the controlled potential of electrolysis.

wave nearly disappeared and the solution appeared to blue. After the 3rd electrolysis at −2.3 volts, the color of solution came more intense. The cyclic voltammograms for the stepwise electrolyzed solution of ABMC to confirm the electrolysis processes were showed at Figure 6. To investigate the fluorescence effects of electrolyzed solution for ABMC, AMC, and coumarin basic molecule were electrolyzed at the controlled potentials (−1.2, −1.8, −2.3 volts) and fluorescence spectra were obtained after stepwise electrolysis.

Electrochemical Fluorescence of Coumarin Derivatives. Acetoxy coumarin derivatives did not show fluorescence before electrolysis, but blue fluorescence was emitted according to controlled potential through electrolysis. At the electrolyzed solution, the fluorescence intensity of coumarin basic molecule (Fig. 7) was low as 950 at −1.8 volts and 1150 at −2.3 volts, but the AMC (Fig. 8) of strong electron releasing substituent (-acetoxy) at 7-position and methyl group at 4-position showed very high intensity as 7000 at −1.8 volts and 9800 at −2.3 volts. Compared with AMC, ABMC (Fig. 9) of substituted the methyl group with weak electron releasing group (-bromo) at 4-position showed reduced fluorescence intensity by cancelling of the acetoxy effect with counterbalancing effect of bromo group.

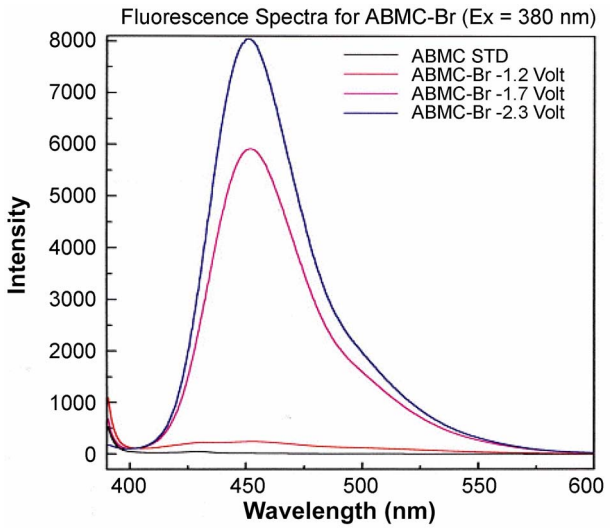


Figure 9. Fluorescence spectra for the ABMC depend on the controlled potential of electrolysis.

Conclusion

The electrochemical reductions of AMC and ABMC were proceeded with the three irreversible steps (−1.2, −1.8, −2.3 volts). EC mechanism consisting of the removal of bromo group at first step, and acetoxy group at the third step was proposed.

Coumarin derivatives have shown blue colored fluorescence by the controlled potential electrolysis at over −1.8 volts. Fluorescence intensity of coumarin attached with electron releasing group was higher than coumarin basic molecule. The fluorescence intensities of AMC and ABMC were enhanced when controlled potential electrolysis was proceeded at more negative potentials as (−2.3 volts). This electrogenerating technique using CPE to obtain enhanced fluorescence compounds will be useful to development for electro-optic materials or laser dyes.

Acknowledgement. This paper was supported by Wonkwang University in 2004.

References

1. Brace, L. *Amer. J. Medical Technology* **1983**, *49*, 457.
2. Lake, B. G. *Archieves of Toxicology* **1984**, *7*, 16.
3. Yuen, S. H. *Analyst* **1978**, *103*, 842.
4. Raw, G. R. *Colaborative International Pesticides Analytical Council* (CIPAC); Heffer, W. & Sons Ltd: Cambridge, U.K., 1970; Vol 1, p 696.
5. Salaman, M. H. *J. Cancer* **1967**, *9*, 177.

6. Hogan, E. C. *Fed. Cosmet. Toxicol*. **1967**, *5*, 141.
7. Moylan, C. R. *J. Phys. Chem*. **1994**, *98*, 13513.
8. Zhang, F. G.; Yu, C. L. *J. Appl. Phys*. **1987**, *62*, 49.
9. Jones, G. II; Rahman, M. A. *J. Phys. Chem*. **1994**, *98*, 13028.
10. Nemkovich, N. A.; Reis, H.; Baumann, W. *J. of Luminescence* **1997**, *71*, 255.
11. Gautier-Thianche, E.; Sentein, C.; Nunzi, J. M.; Lorin, A.; Denis, C.; Raimond, P. *Synthetic Metals* **1997**, *91*, 323.
12. Justin Thomas, K. R.; Lin, J. T.; Tao, Y. T.; Ko, C. W. *J. Am. Chem. Soc*. **2001**, *123*, 9404.
13. Chen, C. H.; Tang, C. W. *Applied Physics Letters* **2001**, *79*, 3711.
14. Kang, S. C.; Oh, S. I.; Kim, K. J. *Bull. Korean Chem. Soc.* **1990**, *11*(6), 505.
15. Huang, Y.; Lu, Z. Y.; Peng, Q.; Xie, R. G.; Xie, M. G.; Peng, J. B.; Cao, Y. *J. of Materials Science* **2005**, *40*, 601.
16. Mal, N. K.; Fugiwara, M.; Tanaka, Y. *Nature* **2003**, *421*, 350.
17. Wang, Z. S. *J. Phys. Chem. B* **2005**, *109*, 3907.
18. Harle, A. J.; Lyons, L. E. *J. Chem. Soc*. **1950**, 1575.
19. Capka, O.; Czech. C. *Chem. Commun*. **1950**, *15*, 965.
20. Zuman, P. *Chem. Listy* **1954**, *48*, 94.
21. Zuman, P. *Organic Polarographic Analysis*; Pergamon Press: New York, 1964; p 251.
22. Zuman, P. *Substituent Effects in Organic Polarography*; Plenum Press: New York, 1967; p 165.
23. Gourley, R. N.; Grimshaw, J.; Miller, P. G. *J. Chem. Soc. (C)* **1970**, 2318.
24. Reddy, B. O.; Reddy, A. V.; Raju, K. M.; Rao, A. K. *J. Electrochem. Soc. India* **1989**, *35*, 319.
25. Partridge, L. K.; Tansley, A. C.; Porter, A. S. *Electrochemical Acta* **1966**, *11*, 517.
26. Bond, A. M.; Thomas, F. G. *Langmuir* **1988**, *4*, 341.
27. Helin, M.; Jiang, Q.; Ketamo, H.; Hakansson, M.; Spehar, A. M.; Kulmala, S.; Ala-Kleme, T. *Electrochimica Acta* **2005**, *51*, 725.
28. Carrazon, J. M. P.; Vergara, A. G.; Garcia, A. J. R.; Diez, L. M. P. *Anal. Chim. Acta* **1989**, *216*, 231.
29. Dempsey, E.; O'Sullivan, C.; Smyth, M. R.; Egan, D.; O'kennedy, R.; Wang, J. *J. Pharm. Biomed. Anal*. **1993**, *11*, 443.
30. Dempsey, E.; O'Sullivan, C.; Smyth, M. R.; Egan, D.; O'kennedy, R.; Wang, J. *Analyst* **1993**, *118*, 411.
31. Wu, Q.; Dewald, H. D. *Electroanalysis* **2001**, *13*, 45.
32. Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; 3rd. Ed.; Pergamon Press: Oxford, 1988; p 69.
33. Zuman, P. *The Elucidation of Organic Electrode Processess*; Acdemic Press: New York, 1969; p 7.