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=단신=

Coumarin 유도체들의 전기화학적 환원과 형광성의 증강

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Enhancement of Fluorescent Properties and Electrochemical Reduction of Coumarin Derivatives

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Abstract : Studies on the electrochemical reduction of 7-acetoxy-4-bromomethyl-coumarin (ABMC), 7-acetoxymethyl coumarin (AMC), and coumarin in 0.1 M tetraethyl ammonium perchlorate acetonitrile solution were carried out with direct current, differential pulse polarography, cyclic voltammetry, and controlled potential coulometry. The electrochemical reduction of ABMC was proceeded through three irreversible steps coupled with the chemical reactions. The solution color was changed to yellow when the carbonyl group was reduced during second step and the color change was independent with bromo group of ABMC. Fluorescent intensity was highest when the electrochemical reduction was controlled at near the overpotential of supporting electrolyte (-2.3 volts).

Key words : coumarin derivatives, differential pulse polarography, cyclic voltammetry, electrochemical reduction, fluorescence.

1. 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. Harle and Lyons[7] have reported that coumarin changes into dimer by polarographic reduction, and Capka[8] has reported the electrochemical reduction and mechanism. Zuman *et al.*[9-11] have investigated a half wave potential and substituent effect for coumarin derivatives and Gourley *et al.*[12] reported that coumarin derivative becomes dihydrocoumarins by the electrochemical reduction in the presence of tertiary amine coumarin, Reddy *et al.*[13] have suggested a polarographic reaction mechanism of 3-acetylcoumarin.

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Partridge *et al.*[14] and Bond *et al.*[15] have explained a phenomenon that coumarin becomes adsorbed to mercury electrode. Diez *et al.*[16] have surveyed the voltammetric determination of coumarin in the emulsified media, and Wang *et al.*[17] have done a differential pulse voltammetric determination with 7-hydroxycoumarin of human urine. Wang *et al.*[18] have made an amperometric biosensor by modifying antibody of 7-hydroxycoumarin with glassy carbon electrode, and have investigated antibody specificity and antibody-antigen interaction kinetic. In recent days, coumarin derivatives are variously applied to chromophore-doped polymer, and become an object of new attention as a nonlinear electro-optic material.[19-23]

In this study, we have performed the electrochemical reduction of coumarin, 7-acetoxmethyl-coumarin (AMC) and 7-acetoxy-4-bromomethyl-coumarin (ABMC) with polarography, cyclic voltammetry, and controlled potential electrolysis method. The electrochemical generating technique as new method for coumarin fluorescence was performed.

2. Experimental

2.1. Reagents

Coumarin derivatives (Aldrich Co.), tetraethylammonium perchlorate (TEAP) and tetraethylammonium hydroxide (TEAOH) were used as purchased. Acetonitrile (AN) was purified by Walter and Ramalay method.[24] Nitrogen gas was passed through basic pyrogallol solution first, calcium chloride layer, and acetonitrile last.

2.2. 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. Emission of 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 A-Line Lab. Thermo Cool was used for temperature control.

2.3. 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 0.1M TEAP-AN solution for 8 min. and also produced 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.

3. Results and Discussion

Diffusion current of coumarin derivatives: In 0.1 M TEAP-AN solution, the typical direct current (DC) and the differential pulse polarograms (DPP) of coumarin, AMC and ABMC were obtained. The polarograms and cyclic voltammograms are shown in *Fig*. 1, and *Fig*. 2, respectively. We were able to interpret that step 1 was bromide reduction of ABMC and step 2 was reductive hydrogenation[7,12] on carbonyl group of coumarin ring. The step 3 was cleavage of ABMC acetoxy group or dihydrogenation of coumarin ring double bond and dimerization process (*Fig*. 1 and *Fig*. 2). In order to know whether each reduction wave is caused by a diffusion wave or 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, DC polarogram was obtained and claculated the percentage[25] of $\Delta i/\Delta T$ by changing the temperature condition of a sample solution at intervals of 5 ℃ from 10 ℃ to 35 ℃

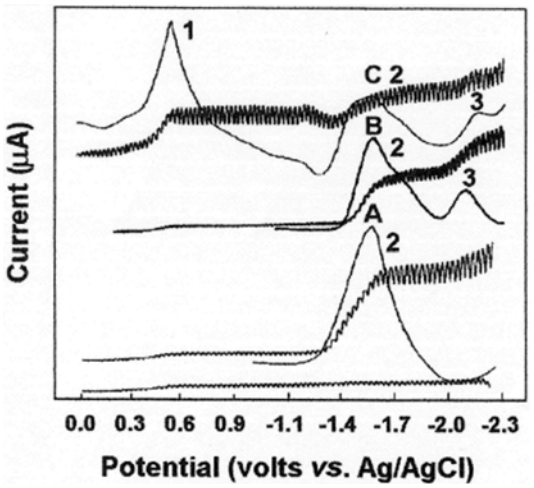


Fig. 1. Typical DC and DP polarogram of coumarin derivatives in 0.1 M TEAP- acetonitrile solution. Scan rate : 50 mV/sec. Current range : 0.02 mA. A : 1×10^{-3} M coumarin, B : 1×10^{-3} M AMC, C ; 5×10^{-4} M ABMC.

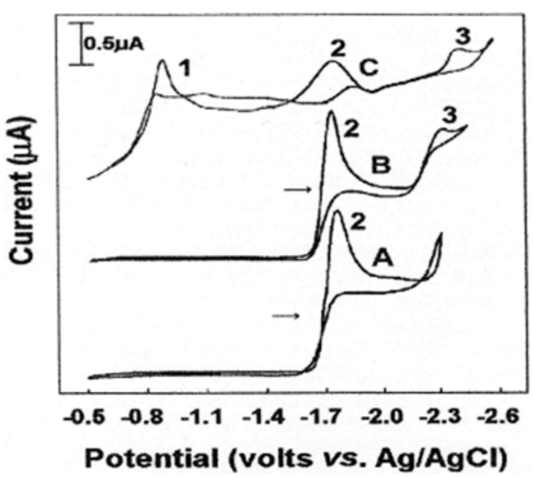


Fig. 2. Typical cyclic voltammograms of coumarin derivatives in 0.1 M TEAP- aectonitrile solution. Scan rate : 50 mV/sec, A : 1×10^{-3} M coumarin, B : 1×10^{-3} M AMC, C : 5×10^{-4} M ABMC.

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. And diffusion current is proportionate to $m^{2/3}t^{1/6}$ according to Ilkovic equation[25]. DC and DP polarograms were obtained by changing drop's life time of mercury drop 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 stage 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 results showed that each reduction stage of ABMC is diffusion controlled ones.

Irreversibility of Electrochemical Reduction of Coumarin Derivatives: Upon the reduction wave of ABMC that showed the three reduction step was investigated. The results of plotting $\log[i/(i_d-i)]$ values of the reduction waves for the changes in potentials are shown in *Fig.* 3. The slope and electron transfer number obtained from the slope of *Fig.* 3 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.* 2) were shown in *Table* 2.

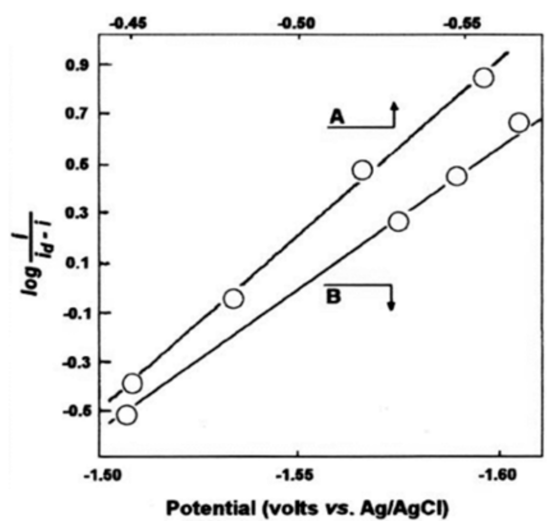


Fig. 3. A plot of log i/ id-i vs. potential from 1×10^{-3} M ABMC polarograms.
A: 1st wave : slope 84 mV, B: 2nd wave : slope 73 mV, 3rd wave : poor DC polarogram to plot

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

Reduction step	-E1/2 (volts vs. Ag/AgCl)	-slope (mV)	$E_{3/4}$ - $E_{1/4}$ (mV)	αn (polarographic electron transfer)	αn (coulometric electron transfer)
1st	0.58	84	82	0.70	1.70
2nd	1.65	73	72	0.81	2.20
3rd	2.25	poor to define		-	0.78

Table 2. Cyclo-voltammetric data for the reduction of 1×10^{-3} M ABMC in 0.1M TEAP- acetonitrile 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 wave	200	-0.94	-	1.75	-	0.53
	100	-0.85	-	1.68	-	0.57
	50	-0.85	-	1.20	-	0.57
2nd wave	200	-2.83	-	1.15	-	0.08
	100	-1.72	-	0.97	-	0.09
	50	-1.72	-	0.60	-	0.08
3rd wave	200	-2.37	-	1.15	-	0.06
	100	-2.31	-	0.97	-	0.06
	50	-2.31	-	0.60	-	0.06

In the plot of polarogram of $\log[i/(i_d-i)]$ *vs.* potentials, the slope value is 59.1/n mV or the potential difference value of $E_{3/4}$-$E_{1/4}$ comes to have one near to 56.4/n mV, the electrode reaction is close to reversibility.[25] An irreversible process can defined as the potential difference value between E_{pc} and E_{pa} becomes larger. For a totally irreverisible 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/αna mV for each tenfold increase in scan rate at 25 ℃.[25] 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/αna mV as scan rate increases, 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. 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 to 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 *Fig*. 4. The peaks potential and current have been almost constantly maintained without a noticeable 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):

For irreversible reduction waves in DC polarogram, we have plotted potential *vs.* $\log[(i_d-i)/i]$, from the slope

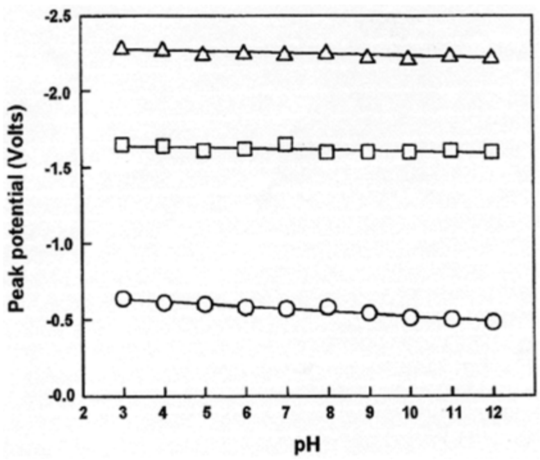
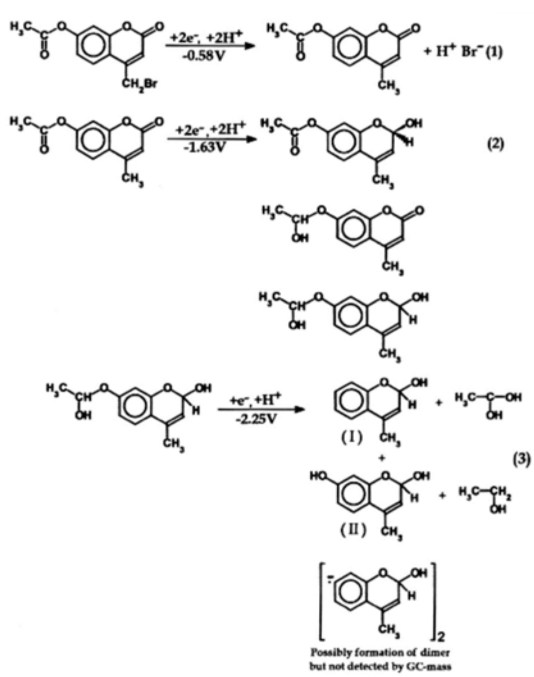


Fig. 4. Effect of pH change in peak potentials of 1×10^{-3} M ABMC in 0.1 M TEAP- acetonitrile solution. ○--○ : 1st wave □--□ : 2nd wave △--△ : 3rd wave.



Scheme 1. The proposed electrochemical reduction mechanism of ABMC.

of which we have obtained αn along with n value obtained by coulometry as shown in *Table* 1. From cyclic voltammetry of ABMC shown in *Fig.* 2, -1.2 volts was selected for the first, -1.7 volts for the second and -2.3 volts for the third electrolysis and controlled potential electrolyzed on mercury pool working electrode with stirring.

After the first 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 one evidence that the bromo group was reduced and removed from ABMC at -1.2 volts. After the second electrolysis at -1.7 volts, the reduction wave nearly disappeared and the solution appeared to fluorescent green-blue. After the third electrolysis at -2.3 volts, the color of solution came more intense. To investigate fluorescence of this electrochemically generated product, ABMC, AMC and coumarin mother molecule were electrolyzed by stepwise at the controlled potentials (-1.2, -1.7, -2.3 volts) and fluorescent spectra were obtained after electrolysis. The cyclic voltammograms for the stepwise electrolysis were compared in *Fig.* 5.

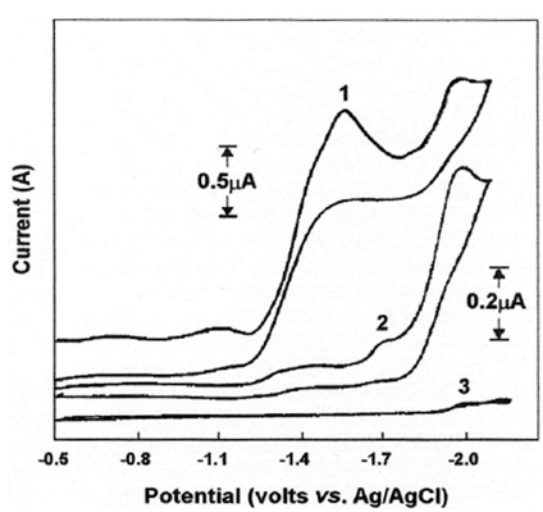


Fig. 5. Cyclic voltammograms in steps of electrolyzed ABMC.
1: after 1st step electrolysis at -1.2 volts, 2: after 2nd step electrolysis at -1.8 volts, 3: after 3rd electrolysis at -2-3 volts.

Electrochemical Fluorescence of Coumarin:

The electrochemically generated coumarin derivatives solution (1×10^{-3} M) were excited at the absorption

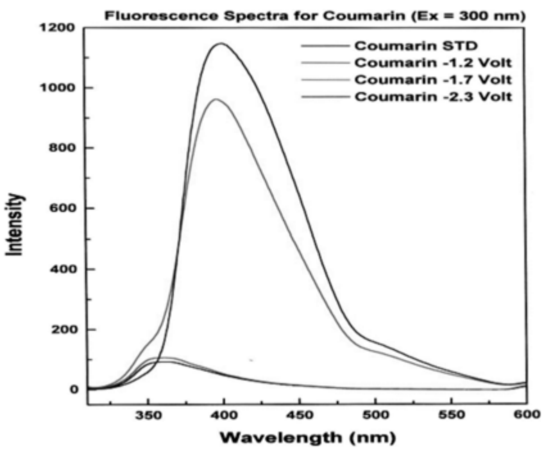


Fig. 6. Fluorescence spectra of coumarin derivates depend upon the electrolysis potential (coumarin).

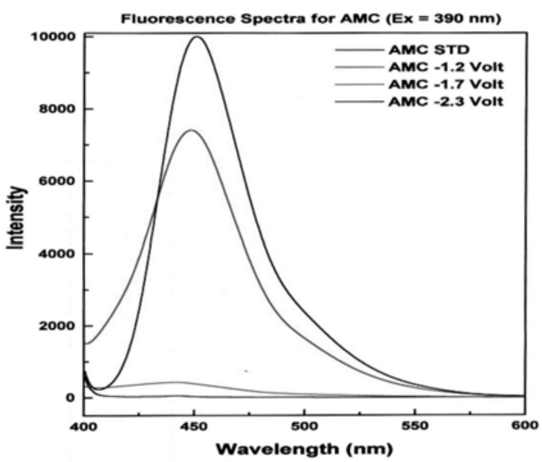


Fig. 7. Fluorescence spectra of coumarin derivates depend upon the electrolysis potential (AMC).

maximum and the fluorescence spectra were compared in *Fig*. 6~8. *Fig*. 6 shows a comparison in fluorescent intensity (a.u) of coumarin mother molecule according to potential of controlled electrolysis. The fluorescent intensities of electrochemically generated coumarin molecule at more negative potential (-1.7, -2.3 volts) were higher than mother molecule. *Fig*. 7 shows the fluorescence intensities of electrochemically generated AMC molecule at more negative potential were higher than AMC. *Fig*. 8 shows the fluorescent intensities of electrochemically generated ABMC molecule at more negative potential were higher than ABMC. Coumarin attached with electron with drawing group showed a stronger fluorescent intensities than coumarin mother molecule.

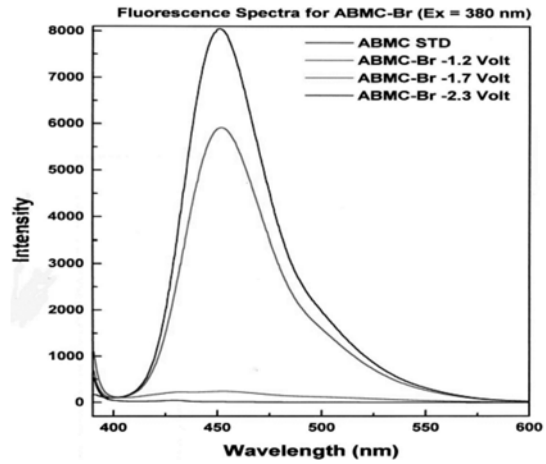


Fig. 8. Fluorescence spectra of coumarin derivates depend upon the electrolysis potential (ABMC).

4. Conclusions

The electrochemical reductions of AMC and ABMC were proceeded as the three steps (-0.6, -1.7, -2.0 volts). first, second and third steps are irreversible processes and a EC mechanism consisiting of the removal of bromo group at the first step, reduction of C=O group to CH-OH at the second step, removal of acetoxy group at the third step, is proposed.

Coumarin derivatives have shown green-blue colored fluorescence by the controlled potential electrolysis at over -1.7 volts. Fluorescent intensity of coumarin attached with electron attracting group was higher than coumarin mother compound. The fluorescent intensities were enhanced strongly when controlled potential electrolysis of AMC and ABMC was proceeded at more negative potential (-1.7, -2.3 volts).

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