BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1391—1394 (1967)

The Direct and Alternating Current Polarography of ε-Aminocaproic Acid and Its Linear Oligomers *via* the Schiff Bases

Yoshinari KOBAYASHI

Nagoya Research Laboratory, Toyo Rayon Co., Ltd., Minato-ku, Nagoya

(Received October 4, 1966)

ε-Aminocaproic acid (ACA) and its linear oligomers were transformed with formaldehyde to the corresponding Schiff bases, which are polarographically active. The a. c. and d. c. polarographic behavior was almost same among ACA, its linear dimer and trimer, of which the half-wave potentials and peak potentials were identical within the range of experimental errors. In d. c. polarography the diffusion current constant was independent of the degree of polymerization, although the peak-current constant in a. c. polarography was influenced by the degree of polymerization and there existed no linear relationship between the concentrations and the peak currents. This electrode reaction was supposed to be a one-electron reduction. In the presence of ε-carprolactam, the *N*-hydroxymethylation of the compound interfered with the appearance of polarographic waves.

The determination of ε-aminocaproic acid (ACA) and its linear oligomers was required for the elucidation of the polymerization mechanism of ε-caprolactam. However, ACA and its linear oligomers them-selves are, like α-aminoacids, polarographically inactive. Several attempts have been reported to transform α-amino-acids into polarographically-active derivatives, such as the corresponding thiocarbamic acids[1] or chelate complexes with cupric ions.[2] Schiff bases were found by Zuman[3] to be polarographically active, and Tur'yan[4] reported on the d. c. polarography of the Schiff bases derived from ω-amino acids with formaldehyde. Tur'yan reported that the distance between amino and carboxyl groups in ω-amino acids affected the half-wave potentials. This stimulated the present author's investigation into the possibility of the simultaneous polarographic determination of ACA and its linear oligomers. The present paper will report on the d. c. and a. c. polarographic behavior of the Schiff bases of ACA and its linear oligomers.

1) K. Lindner, *Acta Chim. Hung.* **26**, 443 (1961).
2) T. Zahradnik and L. Jensovsky, *Chem. Listy*, **48**, 11 (1954).
3) P. Zuman, *ibid.*, **46**, 516, (1952).
4) Ya. I. Tur'yan, Ya. M. Tyurin and B. P. Zhantalai, *Zhur. Anal. Khim.*, **16**, 352 (1961).

Experimental

Apparatus. D. c. and a. c. polarograms were obtained using a Yanagimoto polarograph PA 102 (Yanagimoto Manufacturing Co., Ltd.). The capillary characteristic was 1.27 $mg^{2/3}\,sec^{1/6}$ ($=m^{2/3}\,t^{1/6}$). The measurements were made in an H-type cell at 25± 0.1°C.

Reagents. ACA was obtained by the hydrolysis of ε-caprolactam in diluted sulfuric acid, followed by its neutralization with an aqueous calcium hydroxide solution. After the removal of the calcium sulfate formed, the resultant filtrate was concentrated to dryness and the residue was twice recrystallized from a methanol-water mixture (80 : 20).

The linear dimer and trimer of ACA were prepared by the method described by Zahn.[5] Britton-Robinson's and McIlavaine-Sørensen's buffer solutions were used as the pH-adjusting reagents. A sautrated calomel electrode was used as the reference electrode.

Procedure. Into a 100 m*l* measuring flask, 10 m*l* of a 20% aqueous formalin solution, 10 m*l* of a 1 N sodium hydroxide solution, and a suitable amount of ACA and/or its linear oligomers were added; after the whole solution had then been mixed well, the corresponding Schiff bases were formed within several minutes. The mixed solution was neutralized with 10 m*l* of 1 N sulfuric acid. The pH of the solution was

5) H. Zahn and D. Hildebrand, *Chem. Ber.*, **90**, 320 (1957).

adjusted by the addition of a buffer solution, a diluted sodium hydroxide aqueous solution, or diluted sulfuric acid in order to fill up the volume to 100 ml. Polarograms were obtained after deaeration by bubbling of nitrogen gas.

Results and Discussion

The linear oligomers investigated were limited up to the trimer, because higher oligomers than the trimer had very slight solubility in water.

Effect of pH. The diffusion currents and the half-wave potentials varied greatly with the pH in the d. c. polarography of the Schiff bases of ACA and its linear oligomers. Figure 1 illustrates the dependence of $K=i_d/(h)^{1/2}$, where i_d is the diffusion current and h is the height of the mercury column,

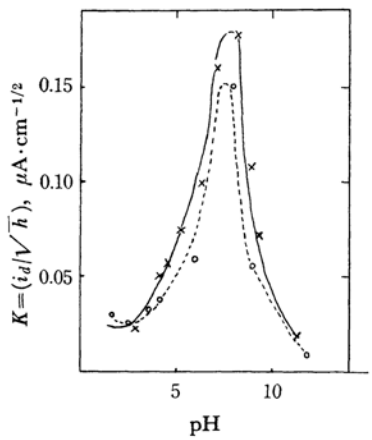


Fig. 1. The dependence of the diffusion currents of ACA and its linear trimer on pH. (Measured at 25°C in 4.0 mM ACA or linear trimer, with heights of mercury column 60, 65 and 70 cm).
—×— ACA --○-- Linear trimer

on the pH in the trimer in comparison with ACA. As the Fig. 1 shows, the diffusion current were at their maximum at pH 7—8. The hydrolysis and formation of Schiff bases are known to proceed through Eqs. (1) and (2):

$$CH_2{=}N{-}R + H_2O \rightleftarrows HO{-}\underset{\displaystyle H}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}{-}NR \qquad (1)$$

$$O^{\ominus}{-}\underset{\displaystyle H}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}{-}\overset{H^{\oplus}}{\underset{|}{N}}R \rightleftarrows H_2C{=}O + RNH_2 \qquad (2)$$

(Where, in this case,
$R=-(CH_2)_5CO[NH(CH_2)_5CO]_mOH$)

In a study of the hydrolysis mechanism of Schiff bases, Jencks[6] reported that, above pH 9, the attack of hydroxide ions on the protonated Schiff bases, as represented by Eq. (1) was the rate-determining step, while below pH 4, the rate-determining step was the decomposition of the tetrahedral addition intermediate, as is shown in Eq. (2). The diffusion currents in d. c. polarography were, therefore, enhanced in the pH region of transition in the rate-determining step. In this region the equilibrium between ACA or its linear oligomers and formaldehyde, represented by Eq. (6), may be supposed to incline towards the right side. The rate of Schiff-base formation reaction was so rapid that the diffusion currents could be observed a few minutes after ACA or its linear oligomers had been mixed with formaldehyde. Their appearance was interfered with aldoxime, ketoxime and hydroxylamine, that is, compounds containing carbon-nitrogen double bonds or compounds which were capable of forming such bonds with formaldehyde. The half-wave potentials in the oligo-ε-caproamide homologue seemed to be independent of the degree of polymerization.

The results were entirely different from those of the ω-amino acid series, where the half-wave potentials were shifted by the carbon number between amino and carboxyl groups. The reason for this may be supposed to be that linear oligo-ε-caproamide homologues were coiled to form helical configurations, as in polypeptides, because they contained amide groups which permitted the formation of a hydrogen bond.

As the pH increased, the half-wave potentials gradually shifted towards the negative side. Figure 2 shows the relationship between the pH and the half-wave potentials of the trimer in comparision with those of ACA.

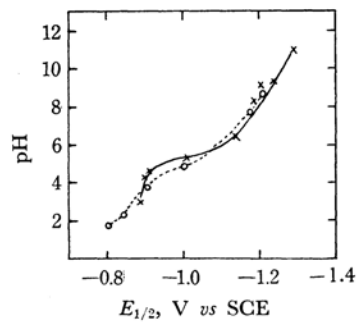


Fig. 2. The dependence of the half-wave potentials of ACA and its linear trimer on pH. (Measured 25°C in 4.0 mM with height of mercury column 65 cm.)
—×— ACA --○-- Linear trimer

All attempts to separate the individual waves based upon each oligo-ε-caproamide homologue were unsuccessful, whether by d. c. or a. c. polarographies or by square-wave or high-frequency polarographies, because the half-wave potentials

6) E. H. Cordes and W. P. Jencks, *J. Am. Chem. Soc.*, **85**, 2843 (1963).

TABLE 1. THE DEPENDENCE OF THE DIFFUSION CURRENTS (i_d) AND THE DIFFUSION CONSTANTS (I_{DC}) UPON THE CONCENTRATION IN THE D. C. POLAROGRAPHY OF THE SCHIFF BASES OF ACA AND ITS LINEAR OLIGOMERS

(Height of mercury column 65 cm, pH 1.6, temp. 25°C)

Concn. mM	Depolarizers: ACA		Linear dimer		Linear trimer	
	Currents i_d, μA	Currents I_{DC}*	Currents i_d, μA	Currents I_{DC}*	Currents i_d, μA	Currents I_{DC}*
2.0	—	—	—	—	0.37	0.225
2.5	0.84	0.267	1.17	0.369	—	—
4.0	—	—	—	—	0.70	0.216
5.0	1.44	0.227	1.86	0.298	—	—
6.0	—	—	—	—	0.97	0.200
7.5	2.15	0.226	2.54	0.286	—	—
8.0	—	—	—	—	1.15	0.178
10.0	2.84	0.224	3.13	0.247	1.32	0.204
12.5	3.28	0.207	3.80	0.239	—	—
15.0	3.90	0.205	4.20	0.220	—	—
Mean		0.226		0.276		0.205

* unit: $\mu A \cdot mM^{-1} \cdot mg^{2/3} \cdot sec^{1/6}$

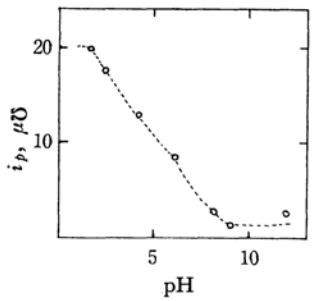


Fig. 3. The dependence of the peak currents of ACA linear trimer upon pH. (Measured at 25°C in 4.0 mM).

of the homologue were too close together. In a. c. polarography the peak currents decrease with the increase in pH. The peak currents and peak potentials were identical in all the homologue investigated.

Figure 3 illustrates the relationship between the peak potentials and the pH in the linear trimer. In the a. c. polarography of ACA and its linear oligomers, the peak currents were not proportional to the concentration.

Calibration. In the calibration, the measurements were carried out in the acid region, where the limiting and peak currents were not greatly influenced by the variation in the pH. The results in the d. c. polarography measured at 25°C are given in Table 1. The diffusion current constants, I_{DC}, were independent of the degree of polymerization.

The results of the a. c. polarography under the same conditions as the d. c. polarography are tabulated in Table 2. The peak-current constants, I_{AC}, which corresponded to the diffusion-current constant were not constant, but varied with the concentrations and with the degree of polymerization.

However, the sensitivity of the a. c. polarography was superior to that of the d. c. polarography. Therefore, the former is more suitable for the analysis of the individual ACA or its oligomers, while it is inadequate for the analysis of mixture.

Electrode Reaction. The irreversible electrode reaction in the d. c. plarography follows Eq. (3):

$$E = E_{1/2} - (RT/\alpha' nF) \ln (i/i_d - i) \qquad (3)$$

where E is the electrode potential; $E_{1/2}$ is the half-wave potential; i is the reduction current; i_d is the diffusion current; n is the number of electrons participating in the reaction, and α' is the constant ($0 < \alpha' < 1$). An analysis of ACA and its linear oligomers based on Eq. (3) is shown in Fig. 4. The $\alpha' n$ value calculated was 0.77.

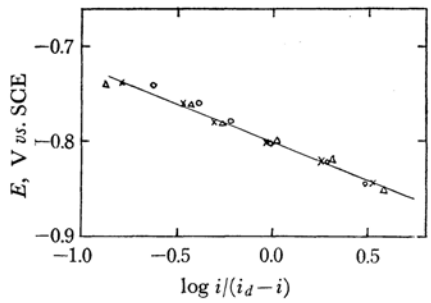


Fig. 4. The relationship between the reduction potentials of ACA and its linear oligomers and the diffusion currents.
× ACA ○ Linear dimer △ Linear trimer

TABLE 2. THE DEPENDENCE OF THE PEAK CURRENTS (i_p) AND THE PEAK CURRENT CONSTANTS (I_{AC}) UPON THE CONCENTRATION IN THE A. C. POLAROGRAPHY OF THE SCHIFF BASES OF ACA AND ITS LINEAR OLIGOMERS

(Measured at same condition as in Table 1)

Concn. mM	Depolarizers: ACA		Linear dimer		Linear trimer	
	Currents i_p, $\mu\mathfrak{V}$	Currents I_{AC}*	Currents i_p, $\mu\mathfrak{V}$	Currents I_{AC}*	Currents i_p, $\mu\mathfrak{V}$	Currents I_{AC}*
2.0	—	—	—	—	14.6	4.22
2.5	26	4.82	22	4.08	—	—
4.0	—	—	—	—	33.6	4.86
5.0	48	4.45	24	2.22	—	—
6.0	—	—	—	—	46.2	4.45
7.5	53	3.28	30	1.99	—	—
8.0	—	—	—	—	54.4	3.93
10.0	86	3.98	26	1.20	60.6	3.50
12.5	58	2.15	25	0.93	—	—
15.0	56	1.73	14	0.43	—	—

* unit: $\mu\mathfrak{V}\cdot mM^{-1}\cdot mg^{2/3}\cdot sec^{1/6}$

TABLE 3. THE DEPENDENCE OF DIFFUSION CURRENTS OF THE D. C. POLAROGRAMS OF THE SCHIFF BASE OF ACA UPON THE PRESENCE OF ε-CAPROLACTAM

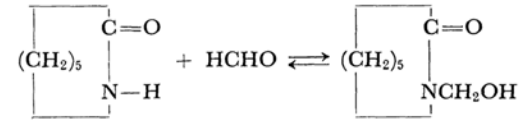
(ACA 1mM; HCHO 0.0535 M; pH 1.6; temp. 21°C)

ε-Caprolactam M	ε-Caprolactam/ACA molar ratio	Diffusion currents μA
0.000	0	3.20
0.001	1	2.85
0.01	10	2.65
0.05	50	1.70
0.10	100	0.00

On the other hand, by Ilkovič's equation n was given as nearly 0.8 when the diffusion constant was calculated according to the Stokes-Einstein equation on the assumption that the densities of ACA and its linear oligomers were nearly unity. Considering these results, the number of electrons participating in the electrode reaction of ACA and its linear oligomers seemed to be unity. Therefore, the electrode reaction may be written as follows:

$$2CH_2{=}N(CH_2)_5CO[NH(CH_2)_5CO]_{m-1}OH + 2e^{\ominus} + 2H^{\oplus} \longrightarrow \begin{matrix} CH_3{-}N(CH_2)_5CO[NH(CH_2)_5CO]_{m-1}OH \\ | \\ CH_3{-}N(CH_2)_5CO[NH(CH_2)_5CO]_{m-1}OH \end{matrix} \quad (4)$$

Effect of ε-Caprolactam. ACA and its linear oligomers are always accompanied by ε-caprolactam and its cyclic oligomers in the polymerization reaction. The lactam reacts with formaldehyde to give *N*-hydroxymethyl-2-oxohexamethyleneimine:[7]



(5)

Therefore, Schiff-base formations (6) from ACA and its linear oligomers are competitive with the *N*-hydroxymethylation of the lactam (5) when the lactam is present:

$$HCHO + H[HN(CH_2)_5CO]_mOH \rightleftarrows CH_2{=}N(CH_2)_3\cdot CO[NH(CH_2)_5CO]_{m-1}OH + H_2O \quad (6)$$

When the molarity of ε-caprolactam was greater than that of formaldehyde, no polarographic wave was observed. Even if formaldehyde was present in an excess amount, the diffusion current decreased as the amounts of ε-caprolactam increased. This indicated that the *N*-hydroxymethylation was undergone more easier than the Schiff-base formation. Table 3 shows the behavior of the decrease in the height of the d. c. polarographic wave of ACA with the increase in the amount of ε-caprolactam.

7) R. E. Bonson and T. L. Thairns, *J. Am. Chem. Soc.*, **70**, 2115 (1948).