Studies on Electrolytic Characteristics of Acetic Acid Formation in Sodium Acetate Electrolysis*

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Electrolysis of sodium acetate to recover HOAc and NaOH is a very interesting problem in the Vinylon (synthetic fiber) industry¹⁾. Great many reports on alkali acetate electrolysis have referred to the Kolbe electro-synthesis²⁾ and the allied reactions (for example, Hofer-Moest reactions³⁾, ester formation⁴⁾, aldehyde formation⁵⁾ and so on) or their reaction mechanisms (for example, discharged ion theory^{2),3)}, acyl peroxide theory^{2),3)} and hydrogen peroxide theory^{2),3)}). However, there are no reports on the recovery of HOAc and NaOH by electrolysis of the NaOAc solution.

The first purpose of this report¹⁾ is to investigate whether the electrolysis to obtain HOAc alone with a high yield is possible or not (excluding Kolbe reaction, Hofer-Moest reaction and so on), from electrolysis of sodium acetate solution. The second purpose is to find out the characteristics of the reaction of HOAc formation and to obtain the suitable anode material, at ordinary electrolytic conditions, considering the appropriate mechanism of anode phenomena.

Fig. 1 is the diaphragm cell, in which the anode is a nickel plate or a magnetite cylinder, and the cathode is mercury⁷⁾. The quantity of electricity was measured by a water coulometer⁸⁾. The electrolysis was carried out at ordinary conditions (NaOAc=200–300 g/l, $D_A=10-15$ A/dm², at room temp.). Gas evolved at the anode was analyzed by means of a Hempel or a Göckel apparatus. Gas absorption was carried out systematically as the following order^{11),12)}.

1. CO₂ (30% KOH sol.), 2. O₂ (alkaline pyrogallol sol.), 3. C₂H₄ (KBr-Br₂ in water), 4. CO (ammonia+Cucl sol.), 5. H₂ (colloidal palladium), 6. C₂H₆ or CH₄ (explosion method with O₂ gas).

Fig. 1 Electrolysis equipment

It was found that the amounts of the gases besides O₂, CO₂ and C₂H₆ were negligibly small through out this experiment. The material loss of acetyl radical (100-S) was calculated by Eq. (4), considering the three main anode reactions Eqs. (1), (2) and (3).

* Studies on the Electrolysis of Sodium Acetate Solution (Part 1)

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$$100-S = \frac{1/4\text{CO}_2}{\text{O}_2 + 1/4\text{CO}_2} \times 10^2$$

(4)

Current efficiency (cE_{ff}), decomposition degree (Z), anodic corrosion (Corr.)⁹⁾ were calculated by analyzing the concentration of HOAc (C_{HOAc}), NaAc (C_{NaOAc}) or Ni^{2+} and Fe^{3+} with the ordinary method.

Table 1-a shows the result of the electrolysis of sodium acetate with nickel anode at ordinary condition.

Table 1-a Electrolysis of Sodium Acetate with Nickel Anode

$\text{NaOAc} = 210 \text{ g/l}$, $D_A = 12.5 \text{ A/dm}^2$, $t = 13-16^\circ\text{C}$

Amount of electricity (A·hr)			1/2	1	1½	2	2½	3	3½	4
Anode compartment	Anode gas	CO ₂ (Vol-%)	15.9	14.2	12.2	11.9	10.4	9.9	9.5	9.3
		O ₂ (")	75.7	79.8	82.2	82.9	85.0	85.5	86.0	86.3
		C ₂ H ₆ (")	8.4	6.0	5.6	5.2	4.6	4.6	4.5	4.4
	Loss of acetyl radical 100-S (%)		5.0	4.3	3.6	3.5	3.0	2.8	2.7	2.6
	Acetic acid (g)		1.023	2.072	3.028	3.946	4.900	5.785	6.527	7.101
	Conc. of acetic acid (N)		0.315	0.691	1.105	1.450	—	2.295	2.602	—
	cE_{ff}^a (1) (%)		94.5	95.7	93.2	91.1	90.5	89.1	86.1	82.0
	cE_{ff}^a (2) (%)		94.5	96.8	88.2	84.9	88.2	81.7	68.2	53.5
	Conc. of sodium acetate (N)		2.254	1.873	1.788	1.640	—	1.214	0.926	—
	Z^a (%)		12.5	26.0	38.3	47.0	—	65.2	73.9	—
Anodic corrosion(mg/A·hr)		4.0	6.0	7.4	7.5	8.4	10.3	10.8	—	
Cathode compartment	NaOH (g)		0.718	1.392	2.129	2.804	3.519	4.028	4.663	5.054
	cE_{ff}^a (1) (%)		99.3	96.6	98.4	97.2	97.7	94.2	92.7	87.5

The material loss of acetyl radical was found to decrease from 5% to 2.5% with decreasing sodium acetate concentration and with increasing HOAc concentration in anolyte. The anodic corrosion of nickel⁹⁾ uprised from 4 mg/A·hr to 11 mg/A·hr with increasing HOAc concentration in anolyte. Electrolytic results for the anodic decomposition degree were plotted in Fig. 2. The anodic current efficien-

Fig. 2 Electrolytic characteristics with a nickel anode

cy was kept high (above 90%) up to 50% of anodic decomposition degree.

Table 1-b shows the anode gas analysis for 1/4 A·hr range (quantity of electricity).

Table 1-b Anode Gas Analysis at the Interval of 1/4 A·hr

(At the Same Electrolytic Condition Table 1-a.)

Amount of electricity (A·hr)	0—1/4	1/4—2/4	2/4—3/4	3/4—1	1—1 1/4	1 1/4—1 1/2	1 1/2—1 3/4
CO ₂ (Vol-%)	14.6	12.7	12.1	10.4	9.7	9.0	10.4
O ₂ (")	68.1	82.7	84.2	86.1	86.5	87.4	86.1
C ₂ H ₆ (")	(17.3)	4.6	3.7	3.5	3.8	3.6	3.5
Amount of electricity (A·hr)	1 3/4—2	2—2 1/4	2 1/4—2 1/2	2 1/2—2 3/4	2 3/4—3	3—3 1/4	3 1/4—3 1/2
CO ₂ (Vol-%)	8.2	8.2	7.9	7.9	7.5	7.1	7.7
O ₂ (")	88.2	88.2	88.8	90.0	89.6	90.0	89.5
C ₂ H ₆ (")	3.6	3.6	3.3	3.1	2.9	2.9	2.8

Magnetite anode showed the same tendency as the nickel anode (Table 2). Anodic corrosion of magnetite anode¹⁰⁾ uprisd from 4 mg/A·hr to 8.5 mg/A·hr with increasing HOAc concentration in the anolyte, but the material loss of acetyl radical was kept constant (about 3%) during the electrolysis. Distribution of sodium in the electrolyzer was plotted in Fig. 3 (magnetite anode) against the quantity of electricity (Na distributes in anolyte as CH₃COONa, in diaphragm as CH₃COONa, in catholyte as CH₃COONa or NaOH and in cathode as amalgam).

Table 2-a Electrolysis of Sodium Acetate with Magnetite Anode

NaOAc=210 g/l, D_A=11.0 A/dm², t=18—22°C

Amount of Electricity (A·hr)			1/2	1	1 1/2	2	2 1/2	3	3 1/2
Anode compartment	anode gas	CO ₂ (Vol-%)	9.8	7.9	10.6	10.8	11.3	11.8	11.8
		O ₂ (")	79.5	85.8	85.0	84.8	85.1	84.8	84.3
		C ₂ H ₆ (")	10.7	6.3	4.4	4.4	3.6	3.4	3.9
		loss of acetyl radical 100-S (%)	2.95	2.25	3.02	3.10	3.20	3.40	3.40
	acetic acid (g)		1.045	2.080	3.119	4.139	5.156	6.088	6.945
	conc. of acetic acid (N)		0.329	0.656	0.986	1.342	1.809	2.349	2.830
	cE _{eff} ^a (1) (%)		96.5	96.1	96.0	95.6	95.3	93.7	91.7
	cE _{eff} ^a (2) (%)		96.5	95.7	96.0	94.3	94.0	86.0	79.2
	conc. of sodium acetate (N)		2.311	2.111	1.905	1.682	1.460	1.263	1.000
	Z ^a (%)		12.5	23.7	34.2	44.0	55.4	65.3	72.0
Cathode compartment	anodic corrosion (mg/A·hr)		4.1	4.5	4.8	5.0	5.5	6.5	8.5
	NaOH (g)		0.694	1.391	2.071	2.757	3.407	4.033	4.610
	cE _{eff} ^c (1) (%)		96.6	96.5	95.8	95.6	94.5	93.0	91.3
	cE _{eff} ^c (2) (%)		96.6	96.3	94.3	95.2	90.0	85.6	81.3
	Z ^c (%)		10.8	20.7	28.6	35.3	—	—	—

Table 2-b Anode Gas Analysis at an Interval of 1/4 A·hr with Magnetite Anode

(At the Same Electrolytic Condition as Table 2-a)

Amount of electricity (A·hr)	0—1/4	1/4—2/4	2/4—3/4	3/4—1	1—1 1/4	1 1/4—1 1/2
CO ₂ (Vol-%)	9.0	12.5	10.2	10.8	11.0	13.6
O ₂ (")	80.1	84.7	86.9	86.3	85.7	84.1
C ₂ H ₆ (")	10.9	2.8	2.9	2.8	3.3	2.3
Amount of electricity (A·hr)	1 1/4—1 1/2	1 1/2—1 3/4	2—2 1/4	2 1/4—2 1/2	2 1/2—2 3/4	2 3/4—3
CO ₂ (Vol-%)	11.7	11.8	12.5	11.5	14.5	11.1
O ₂ (")	85.1	85.1	86.4	85.1	82.8	85.9
C ₂ H ₆ (")	3.2	3.1	1.1	3.4	2.6	3.0

Next, we examined the anode phenomena in order to decrease the material loss of acetyl radical by using various materials as the anode (metal, metal oxide or alloys of iron group metal).

Fig. 3 Distribution of sodium in the electrolyser

Stainless steel (18-11, 18-8, Cr-Ni type) is well known as durable material for acetic acid, dilute mineral acid, alkali etc. and is known to have a low oxygen-overvoltage. On the other hand, platinum is famous as typical anode for the Kolbe and Hofer-Moest reaction.

The current-voltage curves¹³⁾ of NaOAc and H_2SO_4 were shown in Fig. 4 by using stainless steel and platinum anode, the figures on curves showed the decomposition voltage of their salts. From Fig. 4, we find that the anode potentials using Pt anode are higher than those using stainless steel anode at the same current density. The noticeable break or point of inflexion in the curves (probably, critical potential of Hofer-Moest reaction) are visible when the Pt anode and NaOAc was used, but such points disappear in cases of the stainless anode.

	Anode	Cathode
●—●—	18-8 stainless steel	18-8 stainless steel
○—○—	smooth Pt	18-8 stainless steel
△—△—	18-8 stainless	mercury
×—×—	smooth Pt	mercury

Fig. 4 Current-voltage curves and decomposition voltage ($27 \pm 2^\circ\text{C}$) of the solution of 3.66 N-NaOAc and Na_2SO_4

Summary

NaOAc solution was electrolysed with nickel and magnetite anode and with mercury cathode under ordinary electrolytic conditions of the diaphragm cell of a batch system. We found the possibility to obtain HOAc with good yields under ordinary conditions, by using the iron group metal or its alloy anode.

(1) Material loss of acetyl radical were 5~2.5% at nickel anode and constantly ca. 3% at magnetite anode.

(2) Current efficiency was kept very high (above 90%) up to 50% of anodic decomposition degree with both anodes.

(3) Anodic corrosion increased with increase of the concentration of acetic acid, for example, 4 mg/A·hr when HOAc is 0% and 11 mg/A·hr when HOAc is ca. 10% and a Ni anode was used. On the other hand, the corrosion rate was 4 mg/A·hr when HOAc is 0% and 8.5 mg/A·hr when HOAc is ca. 10% and a magnetite anode was used.

(4) Anodic behavior in current-voltage curves of the stainless steel anode was examined, in comparison with that of Pt anode. The anodic potential for the discharge of the hydroxyl-ion (O_2 evolution) was found to be very low (at stainless steel). Finally, the appropriate mechanism of the anode phenomena was discussed.

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Literature :

- 1) S. Okada, T. Eguchi, *Japan. Pat.* 208257 (1954).
 - 2) H. Kolbe, *Ann.* **69**, 279 (1849), *J. Chem. Soc.* **2**, 157 (1850); F. Foerster A. Piguet, *Z. Elektrochem.* **10**, 729 (1904); S. Glasstone, A. Hickling, *J. Chem. Soc.* **II**, 1878 (1934), *Trans. Faraday Soc.* **31**, 1656 (1935); F. Fichter, "Organische Elektrochemie" (1942) Steinkoff, Dresden.
 - 3) H. Hofer, M. Moest, *Ann.* **323**, 284 (1902), *Z. Elektrochem* **10**, 833 (1904); F. Foerster, "Elektrochemie wässriger Lösungen" p. 856 (1923) J. Ambrosius Barth, Leipzig; J. Walker, *J. Chem. Soc.* 2040 (1928); S. Glasstone, A. Hickling, *J. Chem. Soc.* 2345, 2800 (1932), 829 (1933), 10,1772 (1934), 1453 (1936), 325 (1937).
 - 4) J. Peterson, *Z. Physik. Chem.* **33**, 90, 108, 295, 698 (1900).
 - 5) T. Kunugi, *This Journal* **20**, 69, 111, 154 (1952).
 - 6) E.P. Schoch, *Trans. Faraday Soc.* **9**, 274 (1913); W.J. Müller, *Trans. Faraday Soc.* **27**, 736 (1931); "Elektrochemisches Praktikum", (1942), Steinkoff Dresden; E.S. Hedges, *Z. Elektrochem.* **40**, 570 (1934), **41**, 83, 641 (1935), **42**, 166, 789 (1936).
 - 7) J. Samejima, "Butsuri-kagaku Jikkenho" p. 138 (1939), Shōkabō, Tokyo.
 - 8) "Handbook of Electrochemistry" p. 306 (1953) Maruzen, Tokyo.
 - 9) Y. Ōtsuka, "Kihon Kagaku Bunseki" p. 339 (1943), Kyōgokushoten, Kyoto.
 - 10) *Ibid.* p. 473 (1943), Kyoto.
 - 11) S. Glasstone, *J. Chem. Soc.* **II**, 1878 (1934).
 - 12) MacGillivray, *J. Chem. Soc.* **I**, 941 (1932).
 - 13) S. Tanaka, "Denkikagaku Jikkenhō", p. 104 (1957), Uchidarōkakuho, Tokyo.
 - 14) J. Walker, *J. Chem. Soc.* 2040 (1928); S.N. Shukula, J. Walker, *Trans. Farady Soc.* **27**, 722 (1931); J. Walker, J. Weiss, *Trans. Farady Soc.* **31**, 1011 (1935); J. Walker, E. Wild, *J. Chem. Soc.* 207 (1935), 1132 (1937).
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