$$cE_{ff}^a = \frac{v \times 10^2}{v + \frac{n_1^0 D - v}{1 - \exp \{-(n_1^0 D - v)d_1/k_1\}}} = \frac{v}{v + f(v)} \quad (4)$$

$$C_1^0 = \frac{D}{v + \frac{n_1^0 D - v}{1 - \exp \{-(n_1^0 D - v)d_1/k_1\}}} = \frac{D}{v + f(v)} \quad (5)$$

$$v = E.F. - (C.F. + 0.5) \quad (\text{unit: cc/min/900 cm}^2) \quad (6)$$

$$cE_{ff}^a = C_1^0 v / D \times 10^2 \quad (7)$$

① Current efficiency, ② Bath voltage, ③ Power efficiency Anode= 15% Ferro-silicon, current= 90 A, DA=10 A/dm² Temp. = 50-55°C, Overflow ratio of catholyte = 0%, A.F.= 29.5 cc/min/900 cm², Concentration of acetic in feed 300±3g/l

Fig. 5 Kc/N vs power efficiency

Lastly, the relationship between permeability of diaphragm and electric power efficiency⁷⁾ was examined. Here, we adopted Kc/N value as one parameter of permeability, where Kc was the coefficient of permeability, and N was the apparent thickness of diaphragm

$$Kc/N = \frac{V \cdot \eta}{H.S.T} \quad (8)$$

Electric power efficiency, bath voltage and anodic current efficiency were plotted against various Kc/N values in Fig. 5. The electric power efficiency was at maximum between suitable Kc/N values (Kc/N=8-20 poise/hr). This Kc/N values correspond to 2 or 5 times as much as that of A.F. value.

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Studies on the Electrolysis of Sodium Acetate Solution. IV. Studies of Purification of Crude Sodium Acetate

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Sodium acetate (abbreviated as NaOAc) is produced in great quantities by saponification in the

manufacture of vinylon. Such NaOAc is not so sufficiently pure as can be used, without purification, for the mercury cell with diaphragm. The purification method of raw NaOAc is an important problem to be settled before the electrolysis of NaOAc.

NaOAc is produced by the following mechanisms¹⁾ from the polyvinyl acetate (PVAc):

Where R is alkyl radical. Eq. (1) is an ester interchange reaction, Eq. (2) is the direct saponification reaction of PVAc and Eq. (3) is the saponification reaction of alkyl acetate which is produced by an ester interchange reaction (Eq. (1)).

The yield of NaOAc obtained by Eqs. (2) and (3) increased with increasing mole ratio of NaOH to PVAc. Under the ordinary technical condition, 0.2-0.1 mole of NaOAc is produced from 1 mole of PVAc. The filtrate which is separated from polyvinyl alcohol (PVA) (called as "waste liquor of saponification") is feeded in distillation column. Ester and methanol in it are distilled off. The residual liquid in bottom which contains crude NaOAc is ordinarily dark red brown colored owing to organic and inorganic impurities.

The quantity of impurities is usually *ca.* 1% for dry NaOAc, and the chief component of impurities seems to be high polyenaldehyde²⁾ (brown colloidal state, a sort of "aldehyde resin"); the other components are iron compounds or catalyzer of polymerization (azobitrile, ammonium persulfate, benzoyl peroxide etc.). A small quantity of residual vinyl acetate which is contained in saponification liquid system is decomposed to acetaldehyde in the presence of NaOH and the aldehyde seems to be condensed to high polyenaldehyde by repeated aldol-condensation.

These impurities in electrolyte hinder the electrolysis of NaOAc because of the following reasons:

(1). Aldehyde resin is further converted to the dark brown oil or solid by electrolytic oxidation and reduction, which precipitates on and in the filter diaphragm. As the result of it, the electrolytic resistance increases and the percolation rate of flow of diaphragm drops.

(2). Aldehyde resin upraises the surface tension of anolyte and anolyte bubbles out very foamingly.

(3). Metallic impurities which are easily reduced at the cathode (which will not amalgamate with mercury), precipitates of metallic hydroxide (mainly ferric hydroxide, etc.) or poly-condensed aldehyde resin which are floating on the mercury cathode, lower the hydrogen overvoltage of mercury.

In this paper³⁾, the new purification methods of such crude NaOAc were examined, such as adsorption of impurities on adsorbent, recrystallization and dialysis of crude NaOAc solution. The total purification system which was composed of each unit purification process was also considered.

Fig. 1 was the polarograms of various NaOAc solutions which were purified by various methods. The polarogram of NaOAc solution which contained crotonaldehyde resembled that of crude NaOAc solution. The polarogram of the filtrate of crude NaOAc which had been treated with active carbon, resembled that of chemically pure grade NaOAc solution.

The polarograms of various NaOAc solutions to which Ni^{2+} was added, showed the interesting waves as shown in Fig. 2. From Fig. 2, Ni^{2+} seems to form the complex compounds with impurities in crude NaOAc solution, but Ni^{2+} does not form the complex compound with pure NaOAc. Active carbon was very effective for the purification of the impurities of crude NaOAc. Table 1 showed the results of isothermal adsorption of impurities in crude NaOAc by active carbon. The plot of $\log c$ vs $\log x$ was shown by the straight line which was famous for the Freundlich's isothermal adsorption equation⁴⁾ (4).

$$x = X/m = aC^{1/n} \quad (4)$$

Where X is the amount of impurity adsorbed by active carbon, m is the mass of active carbon, C is the concentration of impurity, and a, and $1/n$ are constants.

In practical operation, the necessary amount of active carbon is graphically determined from the equilibrium adsorption curve (same as Fig. 3) and the equation of material balance (Eq. (5)).

$$C_0 V = xm + CV \quad (5)$$

Sample, NaOAc 19 cc (375 g/l) + H₂O 10 cc
Sensibility, 1/5 (③,④), 1/100 (①②)
① Chemically pure grade NaOAc solution (3 times recrystallized from the 1st. class reagent)
② NaOAc solution purified with sufficient active carbon from ③ solution
③ Crude NaOAc (Waste liquor of saponification of PVAc)
④ Mixed solution of chemically pure grade NaOAc solution (① 19 cc) with crotonaldehyde (0.1 cc)

Fig. 1 Polarograms of various NaOAc solutions

Sample, NaOAc 9 cc (300 g/l) + NiSO₄ 1 cc (1/10 N)
Sensibility, 1/1000

Fig. 2 Polarograms of various NaOAc solution with addition of NiSO₄

Table 1 Isothermal Adsorption of Impurities in Crude NaOAc by Active Carbon

Original sample: Brown crude NaOAc solution (NaOAc=300g/l), Amount of used active carbon in each test.: 1.5g,
Dilution rate: Original sample was diluted with pure 300 g/l NaOAc solution.
Temperature: 90°C, Time: 3 hrs.

Dilution rate (fold)	Color before adsorption C ₀ (%)	color after adsorption C (%)	$x = \left(\frac{C_0 - C}{1.5} \right)$ (%/g)	C-value* calculated by Eq. (4) (%)
1.0	100	65.57	22.98	—
1.5	63.67	35.1	21.05	35.1
2.0	50.0	21.5	19.0	22.4
3.0	33.33	10.9	14.9	10.5
4.0	25.0	5.59	13.0	5.5
5.0	20.0	3.425	11.05	3.4
6.0	15.37	2.160	9.55	2.0

* $C = 7.943 C^{0.270}$ (Experimental equation)

Fig. 4 shows the effect of adsorption by the two-steps operation. The necessary amount of active carbon to purify the crude NaOAc solution, (from C=50% to C=5%) is minimum at $C \approx 20\%$ (where C' is the concentration of impurity after the first step adsorption).

Next, the effect of recrystallization of NaOAc was examined. Generally speaking, when the crude NaOAc contains a great amount of impurities, adsorption method is not so effective as recrystallization or dialysis method from the economical and technical standpoints. Sufficient filtration and brief filtration of the properly precipitated crystal from the crude NaOAc solution which contained adequate impurities were carried out in this experiment.

The recrystallization rate was plotted against the necessary amount of active carbon to purify the precipitated crystal in Fig. 5. It was found that the purity of precipitated crystal abruptly dropped

Fig. 3 Isothermal adsorption equilibrium curve of impurities in crude NaOAc by active carbon and graphical determination of necessary amount of active carbon

Volume of original solution=100 cc
Original concentration of impurities: $C_0=50\%$
Final concentration of impurities (after the second-step-adsorption, $C=5\%$)
Concentration of impurities after the first-step-adsorption C' ($C'=5\sim40\%$)

Fig. 4 Determination of minimum quantity of carbon by two-steps-adsorption

at the recrystallization rate more than 60% (sufficient filtration, the case of (A)) or 45% (brief filtration, the case of (B)). The recrystallization rate either 60% (A) or 45% (B) seems to be suitable. Such being the case, the necessary amount of active carbon for the precipitated crystal was only 0.8% for NaOAc (its value corresponded *ca.* 3/100 times as much as that of original crude NaOAc).

Dialysis, which depends on the relative diffusion rate of two solutes, is most efficiently applied to separate low-molecular-weight NaOAc in solution from high-molecular-weight impurities (polyen-aldehydes). The degree of separation or the extent of recovery of low-molecular-weight NaOAc may determine the capacity of the dialysis equipment.

An adaptation of Fick's equation in which the concentration gradient is corrected for the osmotic effect or counterdiffusion of solvent permits calculation of the membrane area. First, assuming that 90% of NaOAc will be recovered and that the concentration will be one-half of the feed concentration (NaOAc 300g/l), the membrane area required to handle 3.0 cc of feed per minute using the parchment paper (Osaka Shiko, Co.) according to Eqs. (6), (7) and (8)⁵⁾ was calculated

$$\frac{V}{UA} = \frac{1-P-r(1-E)}{2.3 E \log [(1-P)/r(1-E)]} \quad (6)$$

where V =feed rate (cc/min.), U =over-all dialysis coefficient $\left(\frac{\text{g/min.}}{(\text{cm}^2)(\text{g/cc})}\right)$, A =membrane area (cm^2), P =ratio of recovered concentration to feed concentration, E =fraction of low-molecular-weight solute passing through the membrane (recovery ratio), Y =ratio of inlet to outlet flow rate on the solution (or feed) side of the membrane.

The values of U and r are calculated from the dialysis coefficient of the solute and the relative diffusion rates of the solute and solvent (in most cases water), respectively.

$$U = \frac{60 D}{0.05 + B/F} \quad (7)$$

where D =diffusion coefficient (cm^2/sec), B = membrane constant, F =hindrance factor.

$$r = \frac{1}{QEC_F + 1} \quad (8)$$

Fig. 5 Recrystallization rate of crude NaOAc solution and the necessary quantity of active carbon to purify the precipitated crystal

- ① Water (in)
- ② Recovered solution (out)
- ③ Feed (in)
- ④ Waste liquid (out)
- ⑤ Membrane of dialysis

Fig. 6 Continuous counter-current dialyzer (140×40×1.5 cm)

Table 2 Dialysis of Crude Sodium Acetate Solution by Using the Continuous Countercurrent Dialyzer

Supplied sodium acetate: NaOAc is 301.6 g/l, polymolecular organic impurity 2.9% (for NaOAc),
Necessary quantity of active carbon to purify: 30% (weight %).
Temperature of dialysis: 5°C, Membrane area: 5500 cm²

Membrane (Parchment paper)		2 sheets of parchment papers			1 sheets of parchment paper	
experiment	No.	No. 1	No. 2	No. 3	No. 4	No. 5
(cc/min)**	×si	0.845	1.325	1.49	1.695	2.70
	×so	1.62	2.71	3.62	3.63	6.70
	×wi	2.225	3.415	4.71	4.535	8.91
	×wo	1.45	2.03	2.53	2.63	4.61
(g/l)	NaOAc in waste	12.6	29.9	25.4	19.0	30.3
	NaOAc in recovered solution	160.9	157.1	139.0	137.8	133.2
(%)	Recovery ratio of solute	91.7	84.0	79.6	83.4	75.2
Q		3.82	4.89	6.47	4.90	7.02
G		2.22	3.42	4.71	4.53	8.61
H		1.67	3.07	4.17	3.92	8.00
ΔX ₁		0.047	0.0371	0.0319	0.0334	0.0307
ΔX ₂		0.0122	0.0254	0.0220	0.0175	0.0234
(cc/min) U		1.15×10 ⁻³	1.13×10 ⁻²	1.39×10 ⁻³	1.97×10 ⁻³	1.78×10 ⁻³
(*)* Necessary quantity of active carbon		1.5	1.0	0.6	0.45	0.5

* Necessary quantity of active carbon to purify the recovered solution (wt-% for NaOAc)

** X_{si}—Inlet quantity of the crude soln. X_{so}—Outlet quantity of the waste soln.

X_{wi}—Inlet quantity of water. X_{wi}—Outlet quantity of recovered soln.

where Q =ratio of diffusion coefficient of solvent to solute ($D_{H_2O}=4.0\times 10^{-5}$ cm²/sec), C_F =concentration of solute in the feed, E =fraction of solute through membrane (=recovery ratio).

In this case, from Eqs. (7) and (8), $U=2.0\times 1.0^{-3}$ cc/min, $r=0.88$. And from Eq. (6)

$$A = \frac{2.3 (0.9) \log (1-0.5)/0.88 (1-0.9)}{1-0.5-0.88 (1-0.9)} \times \frac{3.0}{2.0\times 10^{-3}} = 5.68\times 10^{-3} \text{ cm}^2$$

Fig. 6 is the diagrammatic drawing of continuous countercurrent dialyzer.

For the practical operation of dialyzer and for the accurate controlling of the dialysis, the dialyzer (Fig. 6) was tested under various conditions. The results were treated with Eqs. (9), (10) and (11),⁵⁾ and were summarized in Table 2.

$$\frac{UA}{X_{si}-X_{so}} = \left(\frac{W_{wo}-W_{si}}{G-H} \right)^2 \left\{ \frac{2.3 \log \Delta CX_1 / \Delta CX_2}{\Delta CX_1 - \Delta CX_2} - \frac{Q-1}{2} \left[\frac{G(W_{wo} + W_{wi})(-H(W_{so} + W_{si}))}{(W_{wo} - W_{si})^2} \right] \right\} \quad (9)$$

where Q =ratio of diffusion coefficient of water to solute,

$$G = QX_{wi} + Y_{wi} = QX_{wo} + Y_{wo},$$

$$H = QX_{si} + Y_{si} = QX_{so} + Y_{so},$$

$$\Delta CX_1 = \frac{X_{si}}{QX_{si} + Y_{si}} - \frac{X_{wo}}{QX_{wo} + Y_{wo}}, \quad \Delta CX_2 = \frac{X_{so}}{QX_{so} + Y_{so}} - \frac{X_{wi}}{QX_{wi} + Y_{wi}} \quad (10)$$

$$\text{Recovery ratio of solute} = \frac{X_{wo}}{X_{wo} + X_{so}} \times 10^2 \quad (11)$$

where X and Y refer to the solute and water, respectively and the subscripts s and w refer to the terminal conditions on the solution and water sides of the membrane. Also W_{si} , W_{so} =inlet and outlet total weight of material on solution side. W_{wi} , W_{wo} = inlet and outlet total weight of material on water side.

It was found that the concentration of recovered NaOAc solution was 150 g/l, recovery ratio was 80-90% and recovered solution was very refined. Especially, the necessary amount of active carbon to purify the recovered solution was only 0.5-1.5% for NaOAc. The average values of U were 1.88×10^{-3} at 1 sheet membrane and 1.22×10^{-3} at two sheets membrane.

Summary In order to avoid the electrolytic troubles in mercury NaOAc cell with diaphragm, several purification methods of crude NaOAc which contained organic impurities were tested.

1. Active carbon was the most effective as the adsorbent of organic impurities. Freundlich's equation $x=X/m \text{ ac}^{1/n}$ could be applied for this adsorption.

2. 45%-50% recrystallization rate was suitable in practical operation to obtain pure crystals from crude NaOAc solution.

3. Continuous countercurrent dialyzer was efficiently applied to recover NaOAc from crude NaOAc solution. The degree of recovery was *ca.* 90% and the concentration of recovered solution was one-half of feed concentration. In this case, Lane's dialysis equation⁵⁾ based on weight concentrations and weight flows was sufficiently valid for practical dialysis.

4. The next total purification system, composed of unit purification process, seemed to be relatively rational.

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Studies on the Electrolysis of Sodium Acetate Solution. V. After-treatment of the Anolyte of Sodium Acetate Cell

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A series of purification methods of crude NaOAc was already established in the previous paper¹⁾, which recrystallization, dialysis and adsorption (on active carbon) were used. Thus, the purified NaOAc solution which was obtained by the above method, was effectively electrolyzed for a long period by using a 18 Cr-11 Ni stainless steel anode²⁾, without much loss of acetyl radical and anodic corrosion.

The object of this paper is to find the effective method of HOAc recovery from the electrolyzed anolyte and to remove the metallic ions (Fe^{3+} , Ni^{2+} , CrO_4^{2-} etc.) from the residual raffinate solution (mainly unelectrolyzed NaOAc).

The anolyte which is taken out from the cell, consists of 10% HOAc, 15% NaOAc (unelectrolyzed) and a small quantity of metallic ions. From the economical standpoint, it is difficult to obtain pure HOAc by the distillation of anolyte, because the molecular compounds ($\text{CH}_3\text{COONa} \cdot \text{CH}_3\text{COOH}$, $\text{CH}_3\text{COONa} \cdot 2\text{CH}_3\text{COOH}$ and $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$) will be formed in the distillation still as shown in Fig. 1 and their decomposition temperatures are moderately high.

Mutual solubilities of $\text{CH}_3\text{COOC}_2\text{H}_5$ (solvent) - $\text{CH}_3\text{COOH} \cdot \text{H}_2\text{O}$ (containing NaOAc of various concentrations) system were examined as shown in Table 1.

Fig. 1 $\text{CH}_3\text{COONa} \cdot \text{CH}_3\text{COOH} \cdot \text{H}_2\text{O}$ system
solubility and solid phases (20°C)

Fig. 2 $\text{CH}_3\text{COOC}_2\text{H}_5 \cdot \text{CH}_3\text{COOH} \cdot \text{H}_2\text{O}$ system
equilibrium and tie lines
(water side = 15% NaOAc solution,
20°C)