POLAROGRAPHIC DETERMINATION OF SODIUM CHLORIDE IN COMMON SALT. III.

E D T A Method

Lee Han-Ying and Chen Shih-Shieh

For elimenating the interference of magnesium ion contained in the common salt with the polarographic wave of sodium ion, Lee and Shen used sodium hydroxide to precipitate the magnesium as magnesium hydroxide and determined polarographically the sodium chloride and excess sodium hydroxide as given in the first paper (1). Silver oxide was added to common salt instead of sodium hydroxide in the second paper (2), then silver chloride, magnesium hydroxide and excess silver oxide were precipitated and left only sodium hydroxide in the solution equivalent to the sodium chloride originally contained.

EDTA combines with magnesium and calcium to form soluble chelates that do not give saturated diffusion curve in polarogram, and if EDTA chelates with the magnesium and calcium contained in common salt and the chelates do not interference the polarographic wave of sodium ion, saturated diffusion curve corresponding to sodium chloride only could be measured and a better polarographic determination would be succeeded.

Experimental Work

Chemicals and stock solutions

Distilled mercury, chemical pure $CaCO_3$, chemical pure hydrochloric acid, chemical pure sodium hydroxide, practical reagent grade ethylenediamine tetraacetic acid, Baker analyzed grade sodium chloride, Baker analyzed grade magnesium chloride hexahydrate and baker analyzed grade potassium hydroxide are used. 10.0 g/l NaCl, $MgCl_2$ and $CaCl_2$ solutions, and 0.1 N NaOH solution solution are stock for use.

EDTA sodium salt solutions

2.980 g of EDTA (purity 98%) equivalent to 0.01 M is dissolved in 100 cc, 200 cc, 300 cc and 400 cc of 0.1 N NaOH stock solution, and diluted to 100 ml to give 0.01 F EDTA mono-, di-, tri- and tetrasodium salt solutions respectively.

Chloride mixed solutions

1.0 ml of 10.0 g/l $MgCl_2$ stock solution, 1.0 ml of 10.0 g/l $CaCl_2$ stock solution and 98.0 ml of 10.0 g/l NaCl stock solution, or 2.0 ml of 10.0 g/l $MgCl_2$ or $CaCl_2$ stock

solution and 98.0 ml of 10.0 g/l NaCl stock solution are mixed to be a chloride mixture which contains Nacl 98%, $MgCl_2$ 1% and $CaCl_2$ 1%, or NaCl 98 % and $MgCl_2$ or $CaCl_2$ 2%. 10 ml of this chloride mixture is diluted to 100 ml with the addition of proper amount of EDTA sodium salt stock solution to be a chloride mixed solution which contains 1.0 g/l chlorides.

Poralographic measursment

All experiments were carried out with Sargent-Heyrovsky polarograph Model XII at the following conditions: shunt ratio 100 : I, maximum bridge voltage 3.0 volts, terminal voltage of the cell 3.0 camera ring scale (0.5-0.95), constant temperature 25 ± 0.2 °C and mercury dropping rate 6—8 drop/min. in distilled water.

Polarogram of EDTA or EDTA sodium salt solutions

2ml of EDTA saturated solution and 10 ml of 10.0 g/l NaCl stock solution are taken and diluted to 100 ml. 10 ml of EDTA sodium salt solution aud 10 ml of 10.0 g/l NaCl stock solution are taken and diluted to 100 ml. Polarograms of EDTA or EDTA sodium salts in the presence of NaCl are shown in table I.

Table I Polarogram of EDTA or EDTA salts

EDTA and salts	concentration	pH	Saturated diffusion curve
EDTA	0.01 F	2.0	perfect, $E_{1/2}$=1.68 v
Na-EDTA	0.01 F	4.0	none
Na_2-EDTA	0.01 F	4.5	none
Na_3-EDTA	0.01 F	9.0	none
Na_4-EDTA	0.01 F	10.0	none
HCI	0.01 F	1.0	perfect, $E_{1/2}$=1.68 v

The saturated diffusion curve of EDTA having a half wave potential of 1.68 volts coincides with that of H^+.

Polarogram of chloride mixed solutions

10.0 ml of chloride mixed solution and various amount of EDTA saturated solution are taken and diluted to 100 ml. None saturated diffusion curve is given, as shown in table II.

Table II Polarogram of chloride mixed solution with EDTA

Chloride mixed solution ml	EDTA saturated solution, ml	Saturated diffusion curve
10.0	2.0	none
10.0	4.0	none
10.0	6.0	none
10.0	10.0	none

10.0	15.0	none
10.0	20.0	none

In a pH value as low as 2, alkaline earth EDTA chelates are not formed and neither saturated diffusion curve of H^+ nor that of Na^+ was found. If 10.0 ml of chloride mixed solution and 2 ml of various EDTA sodium salt solution are taken instead of EDTA, saturated diffusion curves were found, as shown in table III.

Table III Polarogarm of chloride mixed solution with EDTA salts

Chloride mixed solution	EDTA salts			pH	saturated diffusion curve
	EDTA,0.0IF	NaOH,0.IN	ratio		
ml	ml	ml	mole		
10	2	0.44	1:2.2	4.5	none
10	2	0.48	1:2.4	4.6	less perfect
10	2	0.56	1:2.8	6.0	less perfect
10	2	0.60	1:3.0	9.0	perfect
10	2	0.80	1:4.0	10.0	more perfect

Though the pH value of the solution decreased very much in the presence of $CaCl_2$ and $MgCl_2$, but it still kept the general rule that the higher the pH value of chloride mixed solution, the better the saturated diffusion curve we got.

EDTA required for alkaline earth EDTA chelates

Various amounts of EDTA trisodium salution are added to 10.0 ml of NaCl-$MgCl_2$-$CaCl_2$ mixed solution and diluted to 100 ml which contains 100 mg or approximately 1.06 m-mol of $MgCl_2$ and 100 mg or approximately 0.90 m-mol of $CaCl_2$. EDTA required for chelation is 1.96 m-mol or 0.01 F EDTA 1.96 ml theoretically. But more than 2.0 ml was needed experimentally, as shown in table IV.

Table IV EDTA required for chelates

Chloride mixed solution ml	Na-EDTA 0.0IF,ml	saturated diffusion curve
10	1.5	irregular
10	1.75	irregular
10	2.00	less perfect
10	2.25	perfect
10	2,50	irregular

Limit of EDTA equivalent

Various amounts of 0.01 F Na_3-EDTA or Na_4-EDTA were. added to 10.0 ml of NaCl-$MgCl_2$-$CaCl_2$ mixed solution to determine experimentally the limit of Na_3-EDTA or Na_4-EDTA equivalent to $MgCl_2$ and CaCl2. Table V shows the results.

Table V Limit of EDTA equivalent

Chloride mixed solution,ml	EDTA salts 0.01F,ml	EDTAsalt:$MgCl_2$+$CaCl_2$	saturated diffusion curve
10	Na_4-EDTA,1.8	I:0.9	none
10	1.9	1:0.95	less perfect
10	2.0	1:1.0	perfect
10	2.1	1:1.05	perfect
10	2.2	1:1.1	none
10	Na_3-EDTA,1.8	1:0.9	none
10	1.9	1:0.95	none
10	2.0	1:1.0	none
10	2.1	1:1.05	none
10	2.2	1:1:1	perfect
10	2.3	1:1.15	perfect
10	2.4	1:1.2	none

For Na_4-EDTA the equivalent is 1.0 mol and for Na_3-EDTA 1.1 mol, 1.0 mol of Na_4-EDTA was taken for the polarographic determination of NaCl and common salt.

Polarogram of chloride mixed solution with Na_4-EDTA

NaCl-$MgCl_2$-$CaCl_2$, NaCl-$MgCl_2$ or NaCl-$CaCl_2$ chloride mixed solution was mixed with equivalent amount of Na_4-EDTA to $MgCl_2$and $CaCl_2$ and polarograms were taken, as shown in table VI.

Table VI Polarogram of chloride mixed solution

	Chemicals	Concentration,F	volume%	ssturated diffusion curve
1	NaCl	0.018	98	perfect
	CaCl2	0.01	1	
	Na4-EDTA	0.01	1	
2	NaCl	0.018	98	perfect
	MgCl2	0.01	1	
	Na_4-EDTA	0.01	1	
3	NaCl	0.018	98	perfect
	$CaCl_2$	0.005	0.5	
	$MgCl_2$	0.005	0.5	
	Na_4-EDTA	0.01	1	

All chloride mixed solutions showed the same polarographic character of Na^+.

Polarogram of chloride-sulfate mixed solution

Equivalent amount of Na_4-EDTA was added to a chloride-sulfate solution contained 0.01 F $MgSO_4$, 0.01 F $CaCl_2$ and 1.0 g/l NaCI. Table VII shows the polarogram.

Table VII Polarogram of chloride-sulfate mixed solution

	Chemicals	Concentration,F	Volume,%	saturated diffusion curve
1	NaCl	0.018	98	perfect
	$CaCl_2$	0.005	0.5	
	$MgSO_4$	0.005	0.5	
	Na_4-EDTA	0.01	1.0	
2	NaCl	0.018	96	perfect
	$CaCl_2$	0.01	1.0	
	$MgSO_4$	0.01	1.0	
	Na_4-EDTA	0.02	2.0	
3	NaCl	0.018	94	perfect
	$CaCl_2$	0.015	1.5	
	$MgSO_4$	0.015	1.5	
	Na_4-EDTA	0.03	3.0	

Na_4-EDTA chelated Mg either in chloride or sulfate salt regardless the total amouut of $MgSO_4$ and $CaCl_2$.

Polarographic character of Na ion

Wave heights of NaCl at various concentratration were measured. The experimental value coincides with the calculated value by taking 1.0g/l NaCl as 100%,as shown in table VIII.

Table VIII Wave height of NaCl

NaCl	Waveheight,mm		
%	experimental	Calculated	difference
100	130.8	130.8	0
98	128.5	128.2	+0.3
96	126.2	125.6	+0.6
94	124.0	123.0	+1.0

In the range of NaCl 95—97% dry base, the difference is small enough to be neglected.

Wave height fraction of Na_4-EDTA

Various equivalent amounts of Na_4-EDTA to $MgCl_2$ and CaClt were added to various kinds of chloride mixed solution. Polarograms of these were taken to determine the wave height fraction corresponding to Na_4-EDTA, as shown in table IX.

Table IX NA_4-EDTA wave fraction

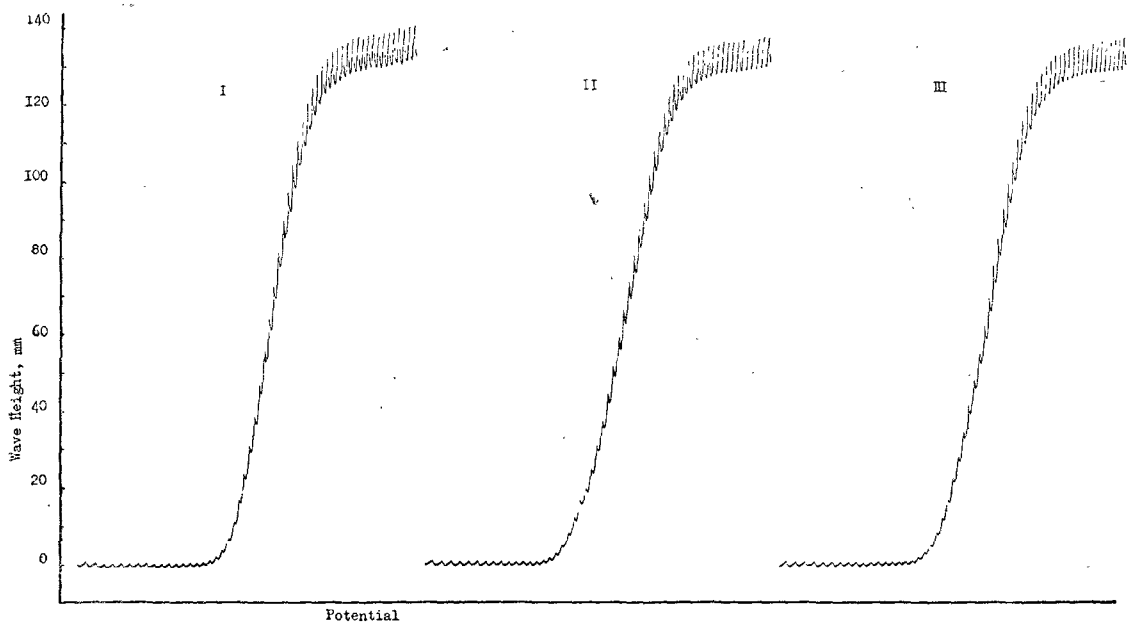
NaCl,ml	Na_4-EDTA,ml	Wave height,mm			
		total	NaCl	Na_4-EDTA	fraction,per 1×10^{-4}F

100	0	130.8	130.8	0	
98	1.0	131.0	128.2	2.8	2.8
96	2.0	131.6	125.6	6.0	3.0
94	3.0	132.4	123.0	9.4	3.1
92	4.0	133.6	124.4	13.2	3.4
					mean 3.06 mm

Wave fraction of Na_4-EDTA calculated = $0.4\times130.8\times58.8/1000$ = 3.05 mm which is in good agreement with the experimental value. A wave height fraction 3.06 mm per 0.4 m-mol of Na_4-EDTA is taken for polarographic measurement.

NaCl determination of common salt

Three solar evaporated salts made by Taiwan Salt Company, one crude two washed are taken for experiment. weighed accurately 2.5 g dried sample, dissolved in water and then diluted to 250 ml to be a solution of 10.0 g/l. 10.0 ml of common salt solution and proper amount of Na_4—EDTA are taken and diluted to 100 ml to determine the Na_4-EDTA requied polarographically. The polarograms are shown in Figure I.



I. Sample I (190) WH=131.0mm, NaCl=98.16% dry base
II. Sample 2 (193) WH=130.4mm, NaCl=97.51% dry base
III. Sample 3 (192) WH=128.9mm, NaCl=96.32% dry dase

Fig. I Current-Potential Curve of 1.0 g/l Common salt

The NaCl content of comon salts are calculated as follows:

Sample I (No. 190)

(1) Sample=2.490 g
Na_4- EDTA required=0.85 ml
Wave height = 129.9 mm
NaCl content = $(129.9\times1.004-0.85\times3.06)/130.8=97.71\%$

(2) Sample = 2.501 g

Na_4-EDTA required = 0.85 ml
wave height=131.0 mm
NaCl content = (131.0−0.85×3.06)/130.8 = 98.16 %
NaCl content, mean wet base = 97.94/101.58 = 96.40 %

Sample 2 (No. 193)

(1) Sample = 2.504 g
Na_4-EDTA required = 0.94 ml
Wave height = 130.6 mm
NaCl content = (130.6×99.84−0.93×3.06)/130.8 = 97.50%

(2) Sample = 2.500 g
Na-EDTA required = 0.93 ml
Wave height = 130.4 mm
NaCl content = (130.4−0.93×3.06)/130.8 =97.51 %
NaCl content,mean wet base = 97.51/102.18 = 95.53 %

Sample 3 (No. 192)

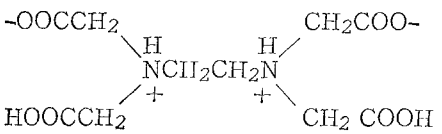
(1) Sample = 2.504 g
Na_4-EDTA required = 0.85 ml
Wave height = 128.9 mm
NaCl content =(128.9×99.84−0.85×3.06)/130.8 = 96.32 %

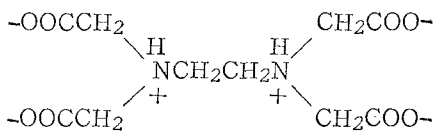
(2) Sample = 2.501 g
Na_4-EDTA required = 0.94 ml
Wave height = 128.7 mm
NaCl content = (128.7−0.94×3.06)/130.8 = 96.19 %
NaCl content,mean wet base = 96.26/106.21 = 90.63

Discussion

Polarographic characters of EDTA and EDTA sodium salts

Since the EDTA molecule contains two amine nitrogen atoms, it can be written in the zwitter-ion form for H_4Y and H_2Y^{2-}(3).



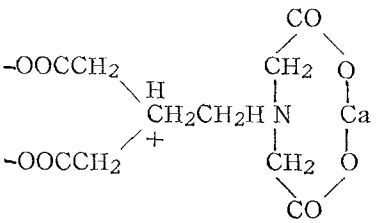


But EDTA saturated water solution gave a saturated diffusion curve of H^+ which half wave potential is 1.68 volts in a pH value of 2.0. It is considerd no zwitter ion was formed. When the pH value is increased by adding alkali to a value of more than 4.0 zwitter ion would be formed. This zwitter ion may accepts reduction and interferes with Na^+ and H^+ to give no saturated diffusion curve.

EDTA alkaline earth chelates

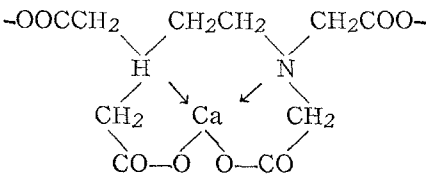
The compound Ca_2H_2Y can be obtained from the reaction of EDTA with calcium

hydroxide or EDTA disodium salt with calcium chloride. In a pH range of 4.0 to 4.5 the dihydrogen calcium compound loses a proton to form the monohydrogen chelated compound $CaHY^-$ (4).



This chelated ion still acepts reduction and interferes with Na^+.

In more alkaline solution when pH is greater than 4.5, the calcium coordinates with both nitrogen forming CaY^{2-} and releasing another proton.



Since this coordinated zwitter ion does not receive reduction, it shows no interference with the diffusion curve of Na^+. That is when equivalent EDTA trisodium or tetrasodium salt to $CaCl_2+MgCl_2$ is added to the chloride mixed solution a saturated diffusion curve is obtained.

Stability of alkaline earth EDTA chelates

Stability constant of alkaline earth EDTA chelates are: Ba^{++} 7.9, Sr^{++} 8.7, Mg^{++} 8.9 and Ca^{++} 10.7 (5). It is in the order of Ba<Sr<Mg<Ca. Stability constant is a function of both the strength of the metal-ligand bond and the acid strength of the protonated ligand. Thus the amount of metal ion which will combine with EDTA at any pH value is a function of the stability constant of the metal chelate and the hydrogen concentration. At different pH value different amount of EDTA costed as shown in table V may be explained.

Bases of polarographic determination

The experimental value of wave height of pure NaCl at various concentrations are in good agreement with the calculated value taken 1.0 g/l NaCl as unity. For the NaCl content in solar evaporvated salt is usually 94—97% dry base, a difference of wave height in 0.6 mm is not serious and may be neglected.

Mixed solution of $NaCl\text{-}MgSO_4\text{-}CaCl_2$ shows the same character as mixed solution of $NaCl\text{-}MgCl_2\text{-}CaCl_2$ in chelating with EDTA, so that the experimental results obtained in chloride mixed solution may be applied to common salt which is a chloride-sulfate mixture.

Since Na_4EDTA is a tetrabasic strong acid (4) and $CaNa_2$-EDTA for the presence of

calcium causes all the four Na^+ to be dissociated readily, this additional Na^+ may be deducted right from the tatal Na^+ given in the polarogram. Even two of them come in the form of NaCl or Na_2SO_4 and two come in the form of NaOH and different anions give different wave heights of Na^+, as EDTA used is only a few per cent in comparing with NaCl, this difference in wave height is small enough to neglect.

Wave height calculation

The wave height of chloride mixed solution is the sum of that of Na^+ combined as NaCl and as Na_4-EDTA. As shown in the experimental work, both Na^+ showed the same polarographic character in wave height, for practical work, therefore, an increase of 3.06 mm in wave height equivalent to 4 m-mol of Na_4-EDTA is used in calculation.

NaCl content in common salt

About equivalent amount of Na_4-EDTA to the alkaline earth contents is added to the common salt solution to check the polarographic wave. If no saturaturated diffusion curve is formed, add 0.02 ml of 0.01 F Na_4-EDTA more to the common salt solution until the diffusion curve is perfect saturated, and take the amount needed. Deduct the additional wave height from the total wave height to get the net wave height cooesponding to NaCl, and then the NaCl percentage is calculated by using the basis that 1.0 g/l NaCl give a wave height of 130.8 mm as 100%. Result of this proposed method compared with NaOH, Ag_2O and chemical methods is given in table X.

Table X NaCl content in common salt

Common salts	Chemical analysis	NaOH method		Ag_2Omethod		EDTA method	
No.	%	%	difference	%	difference	%	difference
1	97.18	96.76	−4.2	96.12	−1.06	96.40	−0.78
2	96.27	95.46	−0.81	95.18	−1.09	95.53	−0.74
3	90.98	91.68	+0.70	89.90	−I.08	90.93	−0.35

Summary

1. In the experimental work of alkaline earth EDTA chelates we found that at a pH value higher than 4.5 both Mg-EDTA and Ca-EDTA chelates are formed, and in the ratio of NaOH : EDTA : $MgCl_2$ or NaOH : EDTA : $CaCl_2$ = 4 : 1 : 1, equivalent amount of EDTA to $MgCl_2$ or $CaCl_2$, and in the ratio of NaOH : EDTA : $MgCl_2$ or NaOH : EDTA : $CaCl_2$ = 3 : 1 : 1 about 1.1 equivalent of EDTA to $MgCl_2$ or $CaCl_2$ is needed. The amount of EDTA required to chelate with the alkaline earth is the same in $MgCl_2$ or and $CaCl_2$, and $MgSO_4$ or and $CaCl_2$.

2. In the NaCl-$MgCl_2$-$CaCl_2$ or NaCl-$MgSO_4$-$CaCl_2$ chloride mixed solution at a pH value higher than 4.5 both $MgNa_2$-EDTA and $CaNa_2$-EDTA chelates dissociate readily to give out all the Na^+, wave height of which is 3.06 mm per 4 m-mol of EDTA in

polarogram.

3. Taking the wave height corresponding to the NaOH added to adjust the pH value to form $MgNa_2$-EDTA or $CaNa_2$-EDTA as the same of that given by NaCl, the net wave height fraction on of NaCl may be calculated from the tatal value by deducting that of the above.
4. By using the chelated action of EDTA with $MgCl_2$ and $CaCl_2$ contained in common salt at a pH value higher than 4.5 the polarogram of three kinds of salar evaporated common salt made by Taiwan Salt Company are measured giving a reault much near to chemical analysis with only a difference of −0.78% max.

Literatures cited

(1) Lee Han-ying, Shen Chen-Sheng, Chemistry, Chinese Chemical Sociaty, No. I, 2 (1956).
(2) Lee Han-ying, Chen Shih-Shieh, Tunghai Journal, Tunghai University, Vol. III, No. 2, 1 (1961).
(3) Kirk-Othmer, Encyclopedia of chemical Technology, Vol. 12, 166 1954 .
(4) Carini Francis F., Martell A.E., Journal of American Chemical Society, Vol. 74, 5745 (1952).
(5) Schnid R.W., Reilly Charles N., Journal of American Chemical society, Vol. 78, 5514 (1956).

食鹽中氯化鈉之極譜定量法 其三
乙烯二胺四乙酸法

李漢英 陳世學

1. 在碱土金屬 EDTA 鉄鹽極譜實驗發見當 pH>4.5 則生成 $MgNa_2$-EDTA 及 $CaNa_2$-EDTA 鉄鹽。在NaOH : EDTA : $MgCl_2$ 或 NaOH : EDTA : $CaCl_2$=4 : 1 : 1 情況下用對 $MgCl_2$ 或 $CaCl_2$ 當量之 EDTA；在 NaOH : EDTA : $MgCl_2$ 或 NaOH : EDTA : $CaCl_2$=3 : 1 : 1 情況下用 1.1 當量之 EDTA. 爲鉄合碱土金屬所用之 EDTA 量與碱土金屬之種類及其鹽之形式無關。
2. 當 pH>4.5 在 NaCl-$MgCl_2$-$CaCl_2$ 氯化物混合溶液中生成之 MgNa-EDTA 及 $CaNa_2$-EDTA 鉄鹽完全解離生 Na^+, 其波高爲 130.8mm 每 1×10^{-4}F Na_4-EDTA。
3. 由 $MgNa_2$-EDTA, $CaNa_2$-EDTA 及用以調節 pH 之 NaOH 所生波高與由 NaCl 所生者相同，故 NaCl 之實波高可由全波高減除上列各項而求得。
4. 利用 EDTA 與 $MgSO_4$ 及 $CaCl_2$ 之鉄合作用在 pH>4.5 下，就臺灣製鹽總廠產三種天日海鹽之 NaCl 極譜定量結果，比 NaOH 法及 Ag_2O 法接近化學法，差額最高−0.78%。