Expansion of Nakano's Results on High Frequency Titration Using the Resistance-type Instrument

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There have been many papers[1-7] on high frequency titration. Many interesting results have been shown by Nakano's paper[8] on this subject. It was based on an experiment using the resistance-type instrument[9]. According to the experimental results of Figs. 2 and 4, which have been obtained by Nakano, the relation between the value of variable resistance, consisting of platinum wire and mercury column, and the concentration of solution shows a minimum point in a case of the condenser-type instrument, and minimum and maximum points in a case of the coil-type instrument. Nakano proved that there exists a relation $\omega C_0 R=1$, at the minimum point for both cases of condenser-type and coil-type instruments. These results and others have been obtained by using the equivalent circuit without the variable resistance which makes a component of the resistance-type instrument. It is, therefore, significant to see if much more accurate results are obtained by using the equivalent circuit with the variable resistance. The present paper is concerned with the results of the calculation of the equivalent circuit containing the variable resistance.

Calculation for Condenser-type Instrument

Fig. 1 shows the equivalent circuit for the components of the portion containing the sample solution (refer to Fig. 7a). This equivalent circuit is the same as the one in Nakano's paper[8] except R_1 referring to the variable resistance of the platinum wire. Therefore, the physical meaning of C, C_0, R and L are omitted. If Z denotes the impedance for the condenser

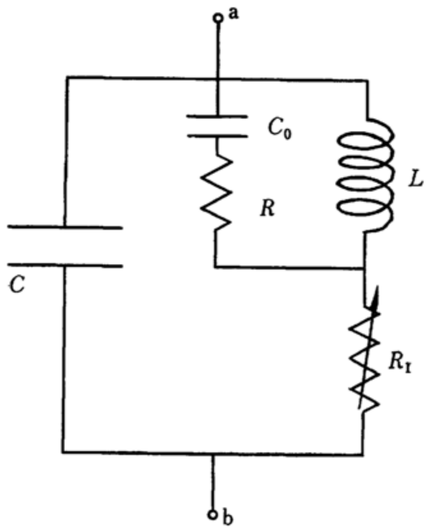

Fig. 1. Equivalent circuit for condenser-type.

element (C_0, R) and the coil (L), the following relation is obtained.

$$\frac{1}{Z}=\frac{(\omega C_0)^2 R}{1+(\omega C_0 R)^2}+\boldsymbol{j}\left\{\frac{\omega C_0}{1+(\omega C_0 R)^2}-\frac{1}{\omega L}\right\} \tag{1}$$

The total admittance between point a and point b in Fig. 1 is written as

$$Y=\boldsymbol{j}\omega C+\frac{1}{Z+R_1} \tag{2}$$

Putting the following expressions for the real and the imaginary parts of $1/Z$

$$A\equiv\frac{(\omega C_0)^2 R}{1+(\omega C_0 R)^2} \quad B\equiv\frac{\omega C_0}{1+(\omega C_0 R)^2}-\frac{1}{\omega L} \tag{3}$$

and for those of Z

$$Z=\frac{A}{A^2+B^2}-\boldsymbol{j}\frac{B}{A^2+B^2}\equiv U-\boldsymbol{j}V \tag{4}$$

the real and imaginary parts of Y can be separated as follows:

$$Y_{\mathrm{real}}=\frac{U+R_1}{(U+R_1)^2+V^2} \tag{5}$$

$$Y_{\mathrm{imag}}=\frac{V}{(U+R_1)^2+V^2}+\omega C \tag{6}$$

1) W. J. Blaedel and H. V. Malmstadt, *Anal. Chem.*, 22, 734 (1950).
2) K. Anderson, E. S. Bettis and D. Revinson, ibid., 22, 743 (1950).
3) P. W. West, T. S. Burkhalter and L. Broussard, ibid., 22, 469 (1950).
4) C. N. Reilley and W. H. McCurdy, Jr., ibid., 25, 86 (1953).
5) S. Fujiwara and S. Hayashi, ibid., 26, 239 (1954); S. Fujiwara and S. Hayashi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 74, 171 (1953).
6) K. Nakano, ibid., 74, 172 (1953).
7) T. Yano, S. Musya, T. Wada and T. Hino, *Chem. Eng.* (*Kagaku Kôgaku*), 20, 339 (1956).
8) K. Nakano, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 75, 776 (1954).
9) K. Nakano, ibid., 74, 227 (1953); K. Nakano, R. Hara and K. Yashiro, *Anal. Chem.*, 26, 636 (1954).

The frequency of oscillation is determined by the assumption that the imaginary part of Y is equal to zero as in the previous paper[8]. Substituting this condition into Fq. 5, one finds

$$(A^2+B^2)R_1=-\frac{Y_{\text{real}}}{\omega C}B-A \tag{7}$$

On the other hand, the change of plate current takes place by putting the beaker containing the aqueous solution into the condenser-type electrode or the coil. In the previous experiment the change of plate current is compensated by adjusting R_1. This manipulation suggests that the value of Y_{real} is kept constant. In the special case when the beaker is empty ($R=\infty$) the values of A and B are 0 and $-1/\omega_\infty L$, respectively. Applying these values to Eq. 7, Y_{real} is obtained as follows:

$$Y_{\text{real}}=R_{1\infty}\frac{C}{L} \tag{8}$$

where $R_{1\infty}$ and ω_∞ denote the variable resistance and the angular frequency in the special case, respectively. Thus Eq. 7 becomes

$$(A^2+B^2)R_1=-\frac{R_{1\infty}}{\omega L}B-A \tag{9}$$

Substituting the above equation into $Y_{\text{imag}}=0$, the following relation between ω and R will be easily obtained:

$$\omega C=-B\frac{1+(A/B)^2}{1+(R_{1\infty}/\omega L)^2} \tag{10}$$

Of course, both Eqs. 9 and 10 should be used simultaneously in order to find how R_1 and ω change with the concentration of solution.

The distributed capacity between the electrode and the solution, C_0, is determined by using the boundary conditions when the beaker is empty or full of the mercury as in the case of Nakano's experiment. From Eq. 10, one obtains

$$\left\{\begin{aligned}\frac{1}{\omega^2{}_\infty L}&=C\left\{1+\left(\frac{R_{1\infty}}{\omega_\infty L}\right)^2\right\}\\ \frac{1}{\omega^2{}_0 L}&=C\left\{1+\left(\frac{R_{1\infty}}{\omega_0 L}\right)^2\right\}+C_0\end{aligned}\right. \tag{11}$$

where ω_∞ and ω_0 are the angular frequency when $R=\infty$ and $R=0$, respectively, and $R_{1\infty}\approx 10\,\Omega$. Hence, the distributed capacity, C_0, is calculated by the following expression:

$$C_0 \doteqdot \frac{1}{\omega_0{}^2 L}-\frac{1}{\omega^2{}_\infty L} \tag{12}$$

which means the same as the method shown in the previous paper[8]. Referring to Table I, of course, it is clear that the following term can be neglected, if $R_{1\infty}$ is 100 Ω and C is 60 $\mu\mu$F:

$$C\left|\left(\frac{R_{1\infty}}{\omega_0 L}\right)^2-\left(\frac{R_{1\infty}}{\omega_\infty L}\right)^2\right|<0.012\ \mu\mu\text{F} \tag{13}$$

Thus the average value of C_0 is 2.3 $\mu\mu$F.

Eq. 9 can be rearranged as follows:

$$\left\{1-\frac{2\omega^2LC_0}{1+(\omega C_0R)^2}+\frac{(\omega^2LC_0)^2}{1+(\omega C_0R)^2}\right\}R_1$$
$$=R_{1\infty}\left\{1-\frac{\omega^2LC_0}{1+(\omega C_0R)^2}-\frac{\omega C_0R}{1+(\omega C_0R)^2}\frac{\omega C_0\omega^2L^2}{R_{1\infty}}\right\} \tag{14}$$

Since the variation of frequency is fairly small as shown by the experiment[10], the frequency can be taken as constant. With this assumption, one differentiates Eq. 14 with respect to R, then puts it equal to zero, and finally obtains the condition which gives the minimum point of R_1

$$R\doteqdot\left(1-\alpha+\frac{\alpha}{\beta}\right)\frac{1}{\omega C_0} \tag{15}$$

where $\alpha\equiv\omega^2LC_0$ and $\beta\equiv\omega C_0\omega^2L^2/R_{1\infty}$.

Neglecting α and α/β which are much smaller than unity according to Table II, one obtains the condition, $\omega C_0R=1$, which is the conclusion of the previous paper[8]. The depth of R_1 at minimum point predominantly depends upon the third term in the right-hand side of Eq. 14. Substituting the condition, $\omega C_0R=1$, into the third term, it becomes $\beta/2$. Then, the following results can be easily found. (a) Using the same coil, the depth of R_1 at minimum point increases with the increase of frequency. (b) Using the same frequency, which is approximately determined by the expression, $\omega^2LC=1$, the depth increases with the increase of L/C. (c) Even though the same frequency is used, the concentration of aqueous solution at the minimum point varies with the salts in solution.

Investigating the results of Fig. 2 in detail, it is noticed that R_1 of curve 9 or 10 is a little larger than $R_{1\infty}$ when the concentration increases.

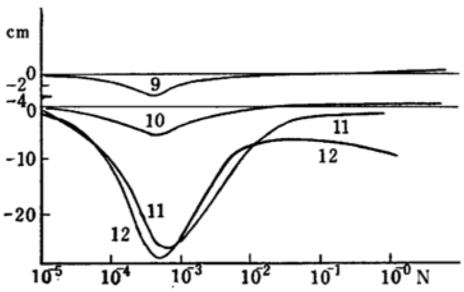

Fig. 2. Relation (Ref. 8) between change of length (resistance) of platinum wire and concentration of salt in aqueous solution for condenser-type.
9, 10, 11 : Ammonium nitrate solution.
12 : Sodium chloride solution.

10) K. Nakano, private communication.

TABLE I

Nos. of turn of coil	Material in beaker	Freq. Kc	ω_∞^2 / ω_0^2	$100^2/\omega_\infty^2 L^2$ / $100^2/\omega_0^2 L^2$	$10^{12}/\omega_\infty^2 L$ / $10^{12}/\omega_0^2 L$	C_0 / p
100	air	1050	4.35×10^{13}	1.24×10^{-3}	53.4_4	2.1_1
($L=4.3\times10^{-4}$H)	mercury	1030	4.19 〃	1.29 〃	55.5_5	
70	air	1280	6.47 〃	1.84 〃	53.3_1	2.6_1
($L=2.9\times10^{-4}$H)	mercury	1250	6.17 〃	1.93 〃	55.9_2	
40	air	1872	1.38×10^{14}	4.28 〃	55.6_2	2.2_6
($L=1.3\times10^{-4}$H)	mercury	1835	1.33 〃	4.45 〃	57.8_8	

TABLE II

No. of curve	Salt	Nos. of turn of coil	L henry	Freq. cycle	ω	α	α/β	$\frac{\omega C_0 \omega^2 L^2}{2\times10}$
9	NH_4NO_3	100	4.3×10^{-4}	1.12×10^6	7.037×10^6	4.90×10^{-2}	3.30×10^{-3}	7.40
10	〃	40	1.3×10^{-4}	1.27 〃	7.979 〃	1.90 〃	9.64 〃	0.986
11	〃	40	〃	1.88 〃	1.181 〃	4.17 〃	6.51 〃	3.20
12	NaCl	70	2.9×10^{-4}	1.26 〃	7.916 〃	4.18 〃	4.35 〃	4.79

This fact is attributed to the second term in the left-hand side of Eq. 14, though the right-hand side of Eq. 14 contains half the value of the same term. It is very desirable to calculate the value of R_1 at the minimum point, which is nearly equal to $R_{1\infty}(1-\beta/2)$. According to Table II, however, they should have a negative value except in the case of curve 10 and this is hard to be explained. Therefore, it is necessary to examine the equivalent circuit again more in detail and the results will be discussed later.

Calculation for Coil-type Instrument

Fig. 3 is considered as the equivalent circuit for the coil-type instrument (refer to Fig. 7b). This equivalent circuit except when including R_1 is the same as the one in the previous paper[8] which contains the element KLR showing the effect of eddy current. According to the same consideration of the equivalent circuit, the following results may be obtained:

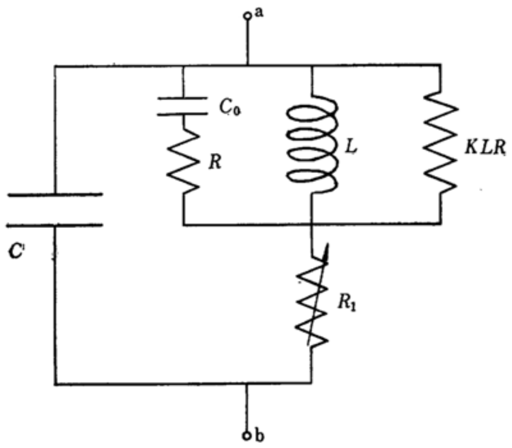

Fig. 3. Equivalent circuit for coil-type.

$$\frac{1}{Z}=\left\{\frac{(\omega C_0)^2 R}{1+(\omega C_0 R)^2}+\frac{1}{KLR}\right\}+\boldsymbol{j}\left\{\frac{\omega C_0}{1+(\omega C_0 R)^2}-\frac{1}{\omega L}\right\}\equiv A+\boldsymbol{j}B \tag{16}$$

$$(A^2+B^2)R_1=-\frac{R_{1\infty}}{\omega L}B-A \tag{17}$$

$$\omega C=-B\frac{1+(A/B)^2}{1+(R_{1\infty}/\omega L)^2} \tag{18}$$

As it is rather difficult to determine the distributed capacity of coil, C_0, by these relations, the value shown in the previous paper[8] will be used in the following discussions.

As mentioned above, the change of frequency is expected to be caused by the change of R. But it is neglected, as the change of frequency was experimentally[10] found to be not so large. After the rearrangement of Eq. 17, it is written as

$$\left\{1-\frac{2\omega^2 LC_0}{1+(\omega C_0 R)^2}+\left(\frac{\omega L}{KLR}\right)^2+\frac{(\omega^2 LC_0)^2(1+2/KL)}{1+(\omega C_0 R)^2}\right\}R_1$$
$$=R_{1\infty}\left\{1-\frac{\omega^2 LC_0}{1+(\omega C_0 R)^2}-\frac{\omega C_0 R}{1+(\omega C_0 R)^2}\frac{\omega C_0 \omega^2 L^2}{R_{1\infty}}-\frac{1}{KLR}\frac{\omega^2 L^2}{R_{1\infty}}\right\} \tag{19}$$

As the first order approximation, the following expression to show the behaviors of all curves for the coil-type instrument is obtained:

$$R_1=R_{1\infty}\left\{1-\frac{\omega C_0 R}{1+(\omega C_0 R)^2}\frac{\omega C_0 \omega^2 L^2}{R_{1\infty}}-\frac{1}{KLR}\frac{\omega^2 L^2}{R_{1\infty}}\right\} \tag{20}$$

The conditions which give the minimum and the maximum points are the same as the one

TABLE III

No. of curve	Nos. of turn of coil	Freq. cycle	ω	C_0 p	α	$\frac{\omega C_0 \omega^2 L^2}{2\times 10}$
2	40	1.45×10^6	9.111×10^6	0.0665	7.18×10^{-4}	0.0425
3	70	〃	〃	0.126	3.03×10^{-3}	0.401
4	100	1.46×10^6	9.173×10^6	0.50	1.81×10^{-2}	3.57
5	100	7.575×10^5	4.759 〃	〃	4.87×10^{-3}	0.498
6	70	9.05 〃	5.686 〃	0.126	1.18×10^{-3}	0.0973
7	40	1.40×10^6	8.796 〃	0.0665	6.69×10^{-4}	0.0382

in the previous paper[8])

$$R=\frac{1}{\omega C_0}\sqrt{\frac{KL-2\pm\sqrt{(KL-2)^2-4(KL+1)}}{2(KL+1)}} \tag{21}$$

where positive and negative signs show minimum and maximum, respectively.

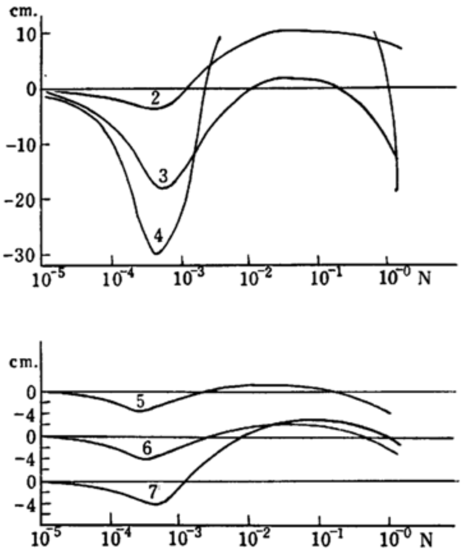

Fig. 4. Relation (Ref. 8) between change of length (resistance) of platinum wire and concentration of sodium chloride in aqueous solution for coil-type.

Investigating the curve in Fig. 4, it is noticed that the maximum value of R_1 is larger than the initial value $R_{1\infty}$. This fact should be ascribed to the second terms of the two sides in Eq. 19. But the value of $\alpha(\equiv\omega^2 LC_0)$ in Table III is too small for this conclusion. In Table III the values of $\beta/2$ $(\equiv\omega C_0\omega^2 L^2/2R_{1\infty})$ which cause the minimum points are smaller than unity except in the case of curve 4.

Re-examination of Equivalent Circuit

It is difficult to understand, for the condenser-type and the coil-type instruments, why the value of $\beta/2$ is greater than unity. The question arises, thus, whether the resistance value of platinum wire at high frequency would be much greater than the value at direct current or not. Even if only the coil-type is taken up, it is difficult to consider that the value at about one megacycle becomes greater than four times the value at direct current. Now, let us consider the loss of coil itself. Assuming that the low resistance, R_l, is connected in series with the inductance of the coil, L, the equivalent circuit for the coil-type instrument becomes Fig. 5, in

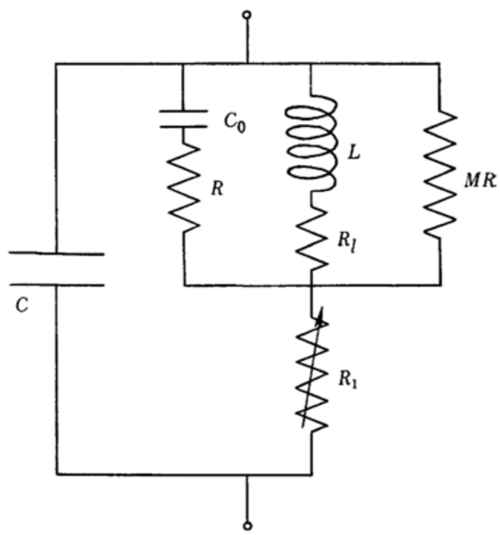

Fig. 5. Equivalent circuit with low resistance showing loss of coil.

which notation, M, means KL. The equivalent circuit for the condenser-type instrument is easily obtained by setting $M=\infty$. Repeating the calculation as before, one obtains

$$\frac{1}{Z}=\left\{\frac{(\omega C_0)^2 R}{1+(\omega C_0 R)^2}+\frac{R_l}{(\omega L)^2+R_l^2}+\frac{1}{MR}\right\}+\boldsymbol{j}\left\{\frac{\omega C_0}{1+(\omega C_0 R)^2}-\frac{\omega L}{(\omega L)^2+R_l^2}\right\}\equiv A+\boldsymbol{j}B \tag{22}$$

$$(A^2+B^2)R_1=-\frac{Y_{\text{real}}}{\omega C}B-A \tag{23}$$

$$\omega C=-B\frac{1+(A/B)^2}{1+(Y_{\text{real}}/\omega C)^2} \tag{24}$$

where

$$Y_{\text{real}}=\frac{C}{L}(R_{1\infty}+R_l)$$

After the rearrangement, Eq. 23 is written as follows:

$$\left\{1-\frac{2\alpha}{1+x^2}+\frac{2\alpha xQ^{-1}}{1+x^2}+\frac{2\alpha Q^{-1}}{Mx}+\frac{\alpha^2(1+Q^{-2})}{(Mx)^2}+\frac{\alpha^2(1+Q^{-2})(1+2/M)}{1+x^2}\right\}R_1$$
$$=R_{1\infty}\left\{1-\frac{\alpha(1+Q^{-2})(R_{1\infty}+R_l)}{(1+x^2)R_{1\infty}}-\frac{x}{1+x^2}\,\frac{\omega C_0(\omega L)^2(1+Q^{-2})}{R_{1\infty}}-\frac{\omega C_0(\omega L)^2(1+Q^{-2})}{MxR_{1\infty}}\right\} \tag{25}$$

where $x\equiv\omega C_0R$, $\alpha\equiv\omega^2LC_0$ and $Q^{-1}\equiv R_l/\omega L$.

In Eq. 25, the term which gives the minimum value for the resistance R_1 is the same as the one in Eq. 19 except for the factor, $1+Q^{-2}$, being greater than unity. Therefore, it seems impossible in this procedure to find that the term in question has a value smaller than unity.

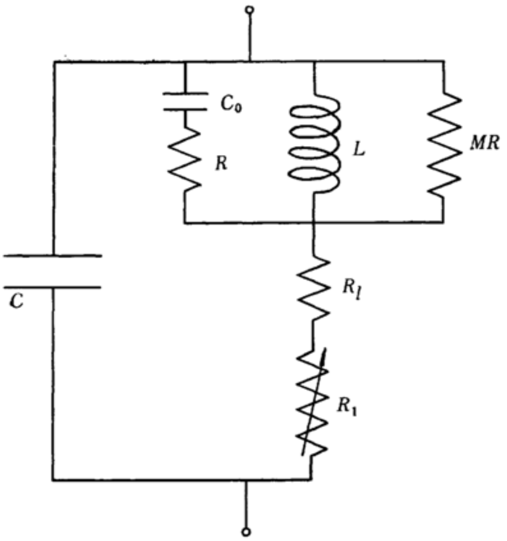

Fig. 6. Another equivalent circuit with low resistance showing loss of coil.

Now, Fig. 6 is considered instead of Fig. 5. In Eq. 19, substituting as follows $R_1\to R_1+R_l$, $R_{1\infty}\to R_{1\infty}+R_l$, the following equation is obtained:

$$\left\{1-\frac{2\omega^2LC_0}{1+(\omega C_0R)^2}+\left(\frac{\omega L}{MR}\right)^2+\frac{(\omega^2LC_0)^2(1+2/M)}{1+(\omega C_0R)^2}\right\}(R_1+R_l)$$
$$=(R_{1\infty}+R_l)\left\{1-\frac{\omega^2LC_0}{1+(\omega C_0R)^2}-\frac{\omega C_0R}{1+(\omega C_0R)^2}\,\frac{\omega C_0\omega^2L^2}{(R_{1\infty}+R_l)}-\frac{\omega^2L^2}{MR(R_{1\infty}+R_l)}\right\} \tag{26}$$

The Q of the coil shows $\omega L/R_l$ and then R_l is calculated from Q at the corresponding frequency. Two cases[10] are considered for the Q of the coil. One of them is to measure only the coil, and the other case is to measure the coil containing distilled water. The former should be considered for the condenser-type instrument, whereas the latter for the coil-type instrument with the assumption that the loss by distilled water is contained in $Q(=\omega L/R_l)$. In Table IV the values of the terms in question for the coil-type instrument are less than unity. The resistance value of platinum wire is 0.2 Ω/cm. and $M\approx10^3$ as shown in the previous paper[8]. The calculated values of the depth at minimum point agree with the experimental values in the case of curves 3 and 6 in Table IV. But the values of curves 4 and 5 are too great in comparison with the experimental ones, though the values of curves 2 and 7 are not discussed.

The calculated values for the condenser-type instrument are shown in Table V. In this case, the values of the terms in question become smaller than the previous value, but some of them are still greater than unity. Therefore, this equivalent circuit seems not to be useful

TABLE IV

No. of curve	ωL	Q*	R_l	$\frac{\omega C_0\omega^2L^2}{2(R_{1\infty}+R_l)}$	Depth** of curve		Exp. value
					Ω	cm.	
2	1186	68.0	17.4	0.0155	−0.415	−2.07	−4.0
3	2642	77.5	34.1	0.0908	−3.95	−19.7	$-18._5$
4	3944	91.5	43.1	0.672	−35.7	−179	−31
5	2046	119.5	17.1	0.184	−4.94	−24.7	−3.5
6	1648	88.0	18.7	0.0339	−0.956	−4.78	−4.0
7	1143	68.0	16.8	0.0143	−0.374	−1.87	−4.5

* According to K. Nakano[10]

** $(R_1)_{\min}-R_{1\infty}\fallingdotseq(R_{1\infty}+R_l)\left\{\frac{\alpha}{2}-\frac{\omega C_0\omega^2L^2}{2(R_{1\infty}+R_l)}\right\}\Big/(1-\alpha)$

for the calculation of the depth of the condenser-type instrument, though Q is the value of the coil without the condenser-type electrode.

TABLE V

No. of curve	ωL	Q*	R_l	$\frac{\omega C_0\omega^2 L^2}{2(R_{1\infty}+R_l)}$
9	3026	112.8	26.8	2.01
10	1037	71.5	14.5	0.403
11	1535	67.8	22.6	0.982
12	2296	88	26.1	1.33

* According to K. Nakano[10]

The calculation on high frequency titration has been extended on the basis of Nakano's paper[8]. As a result of calculation, the relation between the variable resistance, R_1, and the high frequency resistance, R, having some connection with the concentration of solution becomes clear in some degree, including the condition, $\omega C_0 R=1$. The term $\omega^2 LC_0/1+(\omega C_0 R)^2$, seems to cause the fact that R_1 becomes greater than $R_{1\infty}$ in the case of concentrated solution. Some of the calculated values of depth at minimum point are considerably great in comparison with the experimental one in the case of the coil-type instrument and can not be obtained in the case of the condenser-type instrument. Hence, it seems necessary to take into account another factor in the calculation of the equivalent circuit in order to obtain better agreement with the experimental results.

The sample solution in the condenser-type electrode or the coil has the capacitance together with the resistance as shown in Nakano's paper[8]. The former was omitted in Nakano's paper, under the assumption that the effect of the former is negligible when the value of the latter is not so great. Now, let us consider the equivalent circuit (Fig. 8) on the basis of Figs. 7a and 7b. This equivalent circuit is of the same physical meaning as in the case of Fig. 5 except in the case of the capacitance, $\varepsilon' C_1$, C_2, which are visualized by Figs. 7a and 7b, where the notation ε' means the dielectric constant (real part) of the sample solution. As mentioned above, the sample solution in the condenser-type electrode or the coil has the capacitance, which is shown by the notation $\varepsilon' C_1$ in Figs. 7a or 7b (and Fig. 8) instead of C_1 in Nakano's paper. The notation C_2 shows the rest of the capacitance of the condenser-type electrode in Fig. 7a and the rest of the self capacitance of the coil in Fig. 7b, which has also been shown by C_3 in the recent paper[11].

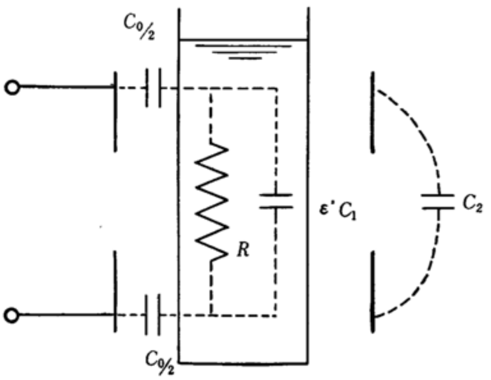

Fig. 7 (a). Relation between sample solution in condenser-type electrode and equivalent circuit.

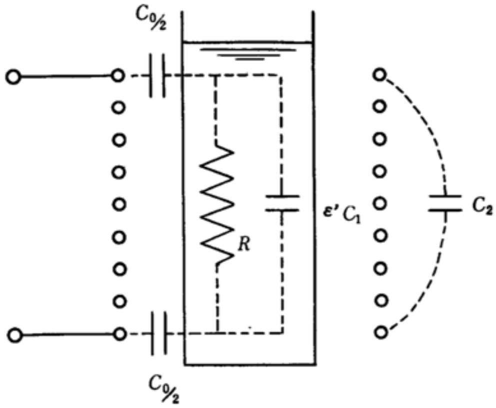

Fig. 7 (b). Relation between sample solution in coil and equivalent circuit.

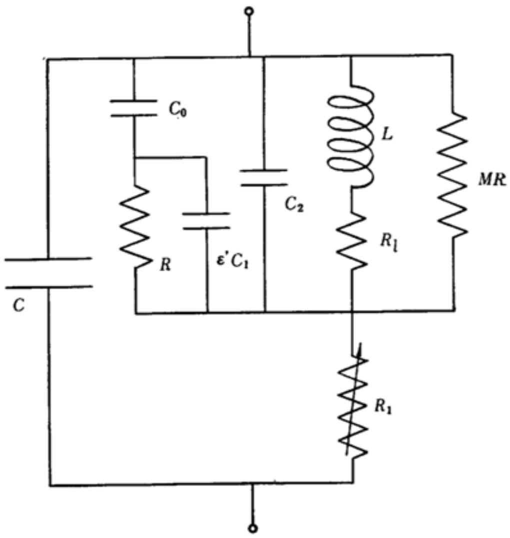

Fig. 8. Equivalent circuit taking into account another factor.

Again one repeats the similar calculation of this equivalent circuit containing another factor $\varepsilon' C_1$ and C_2. As a result of calculation, the following equation is easily obtained:

11) P. F. Knewstubb and T. M. Sugden, *Trans. Faraday Soc.*, **54**, 372 (1958).

$$\frac{1}{Z}=\left\{\frac{(\omega C_0)^2 R}{1+\omega^2(\varepsilon' C_1+C_0)^2R^2}+\frac{R_l}{R_l^2+(\omega L)^2}+\frac{1}{MR}\right\}$$
$$+\boldsymbol{j}\left[\frac{\omega C_0\{1+\omega^2\varepsilon' C_1(\varepsilon' C_1+C_0)R^2\}}{1+\omega^2(\varepsilon' C_1+C_0)^2R^2}\right.$$
$$\left.+\omega C_2-\frac{\omega L}{R_l^2+(\omega L)^2}\right]\equiv A+\boldsymbol{j}B \tag{27}$$

$$(A^2+B^2)R_1=-\frac{Y_{\text{real}}}{\omega C}B-A \tag{28}$$

$$\omega C=-B\frac{1+(A/B)^2}{1+(Y_{\text{real}}/\omega C)^2} \tag{29}$$

$$Y_{\text{real}}=\frac{C}{L}\frac{\{1-2\alpha_\infty+\alpha^2{}_\infty(1+Q_{\infty 1}^{-2})\}R_{1\infty}+R_l}{1-\alpha_\infty(1+Q_{\infty 1}^{-2})} \tag{30}$$

where $Q_{\infty 1}\equiv\omega_{\infty 1}L/R_l$, $\alpha_\infty\equiv\omega^2{}_{\infty 1}L\left(C_2+\frac{C_0C_1}{C_1+C_0}\right)$, $\omega_{\infty 1}$ and $R_{1\infty}$ are the angular frequency ω and the variable resistance R_1, when $R=\infty$ and $\varepsilon'=1$, respectively. After the rearrangement of Eq. 28, it is written as the following expression corresponding to Eq. 25:

$$\left[1-2\alpha_2+\alpha_2^2(1+Q^{-2})-\frac{2\alpha(1+qx^2)}{1+x^2}\right.$$
$$+\frac{2\alpha p x Q^{-1}}{1+x^2}$$
$$+\frac{2\alpha\{\alpha_2(1+qx^2)+p\omega L/M_0\}(1+Q^{-2})}{1+x^2}$$
$$+\frac{\alpha^2(1+Q^{-2})\{(px)^2+(1+qx^2)^2\}}{(1+x^2)^2}$$
$$\left.+\frac{2Q^{-1}\omega L}{M_0 x}+\left(\frac{\omega L}{M_0 x}\right)^2(1+Q^{-2})\right]R_1$$
$$=\frac{\xi R_{1\infty}+\eta R_l}{1-\eta}\left[1-\frac{\xi R_{1\infty}+R_l}{\xi R_{1\infty}+\eta R_l}\left\{\alpha_2+\frac{\alpha(1+qx^2)}{1+x^2}\right\}\right.$$
$$\left.\times(1+Q^{-2})-\left(\frac{\alpha p x\omega L}{1+x^2}+\frac{\omega^2L^2}{M_0x}\right)\frac{(1+Q^{-2})(1-\eta)}{\xi R_{1\infty}+\eta R_l}\right] \tag{31}$$

where

$$x\equiv\omega(\varepsilon' C_1+C_0)R,\ Q\equiv\omega L/R_l,$$
$$M_0\equiv M/\omega(\varepsilon' C_1+C_0)$$
$$p\equiv\frac{C_0}{\varepsilon' C_1+C_0},\quad q\equiv\frac{\varepsilon' C_1}{\varepsilon' C_1+C_0}$$
$$\alpha\equiv\omega^2 LC_0\qquad \alpha_2\equiv\omega^2LC_2$$
$$\xi\equiv1-2\alpha_\infty+\alpha^2{}_\infty(1+Q_{\infty 1}^{-2}),\ \eta\equiv\alpha_\infty(1+Q_{\infty 1}^{-2})$$

Thus, the term in question becomes

$$\frac{\alpha p x\omega L}{1+x^2}\frac{1+Q^{-2}}{R_{1\infty}} \tag{32}$$

assuming that ξ and η are approximately equal to unity and zero, respectively. It seems that the condition giving the minimum point is almost entirely determined by this term taking the rest into account. This term contains the significant factor p, which contains $\varepsilon' C_1$ and C_0, as compared to the corresponding term in Eq. 25. The capacitance of the sample solution, $\varepsilon' C_1$, will be comparable to or larger than C_0, when the sample solution is an aqueous solution which has a large value of dielectric constant, though C_1 is considerably smaller than C_0. Thus, it is possible to find the possibility that the factor p has a value somewhat smaller than unity, since the capacitance of the sample solution, $\varepsilon' C_1$, can not be neglected in comparison with the capacitance C_0. It seems likely that the consideration of the factor, $\varepsilon' C_1$, is helpful for the solution of the problem being discussed in this paper.

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