Analysis of Variation of Coil Character by Aqueous Solution with Q-Meter

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It is interesting in many respects to notice how the character of a circuit is changed by inserting a substance into its condenser-type electrode or its coil. Several papers[1-10] have been reported already, and especially the effect of an aqueous solution, for high frequency titration, has been studied by many investigators[11-27]. In Ref. 25, a description was given, showing that the resistance of aqueous solution was used as an important factor for explaining the effect caused by the aqueous solution. It was based on an experiment using the resistance-type instrument shown in Ref. 26.

Recently the relationship between the variable

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1) P. W. West et al., *Anal. Chem.*, **23**, 1625 (1951).
2) B. W. Thomas et al., ibid., **23**, 1750 (1951).
3) F. W. Jensen et al., ibid., **23**, 1770 (1951).
4) P. H. Monaghan et al., ibid., **24**, 193 (1952).
5) P. W. West et al., ibid., **24**, 1250 (1952).
6) M. Honda, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **73**, 529 (1952); **74**, 371 (1953).
7) D. G. Flom et al., *Anal. Chem.*, **25**, 541 (1953).
8) T. Yano, S. Musya, T. Wada and T. Hino, *Chem. Eng.* (*Kagaku Kōgaku*), **20**, 339 (1956).
9) F. J. Schmidt, *Anal. Chem.*, **29**, 1060 (1957).
10) P. F. Knewstubb et al., *Trans. Faraday Soc.*, **54**, 372 (1958).
11) F. W. Jensen et al., *Ind. Eng. Chem., Anal. Ed.*, **18**, 595 (1946).
12) W. J. Blaedel et al., *Anal. Chem.*, **22**, 734 (1950).
13) K. Anderson et al., ibid., **22**, 743, 1272 (1950).
14) W. J. Blaedel et al., ibid., **22**, 1410 (1950).
15) J. L. Hall et al., ibid., **23**, 966 (1951).
16) F. W. Jensen et al., ibid., **23**, 1327 (1951).
17) J. L. Hall, ibid., **24**, 1236, 1244 (1952).
18) O. I. Milner, ibid., **24**, 1247 (1952).
19) S. Musya, M. Itō and M. Takeda, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **73**, 482 (1952).
20) S. Fujiwara and S. Hayashi, ibid., **74**, 171 (1953).
21) K. Nakano, ibid., **74**, 172 (1953).
22) C. N. Reilley et al., *Anal. Chem.*, **25**, 86 (1953).
23) S. Fujiwara and S. Hayashi, ibid., **26**, 239 (1954).
24) K. Nakano, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 494, 773 (1954); **76**, 1096 (1955); **77**, 551 (1956).
25) K. Nakano, ibid., **75**, 776 (1954).
26) K. Nakano, ibid., **74**, 227 (1953); K. Nakano, R. Hara and K. Yashiro, *Anal. Chem.*, **26**, 636 (1954).
27) K. Nakano and S. Shibata, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 223 (1955).

resistance and the resistance of aqueous solution at high frequency was clarified to some extent[28]. In that calculation, the equivalent circuit containing the variable resistance and the other factors was used. However, the value of the distributed capacity of coil, C_0, could not be obtained by the equation for the coil-type instrument. Then, the value shown in Ref. 25 was used. In the present paper both the method, measuring the distributed capacity of coil, and the results of calculation for the variations of Q and C, which are based on the previous papers[28-30], will be described for the case of coil using the Q-meter.

Experimental

The Q-meter system used in this experiment is shown in Fig. 1. A voltage stabilizer is employed for the Q-meter. The curve of V/V_0 vs. C, as shown in Fig. 2, is obtained at a constant frequency, f, when the capacity of the variable condenser is changed. When an aqueous solution is inserted into the coil, this curve shifts to the dotted line, as is also shown in Ref. 29. The variation of coil character is visualized by these curves. Then the quality of a coil (Q) is defined by the maximum value of V/V_0. In the present paper, assuming that these curves are symmetric, the capacity of condenser at tuning point (or the tuning capacity) is calculated by taking an average of two values (C', C'' in Fig. 2), at which the values of V/V_0 are equal to each other. This method is convenient since the precise value can be easily obtained in comparison with another method.

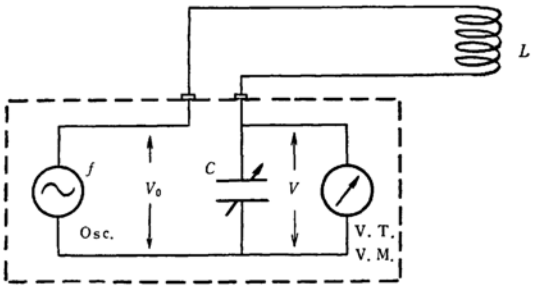

Fig. 1. Q-Meter and coil.

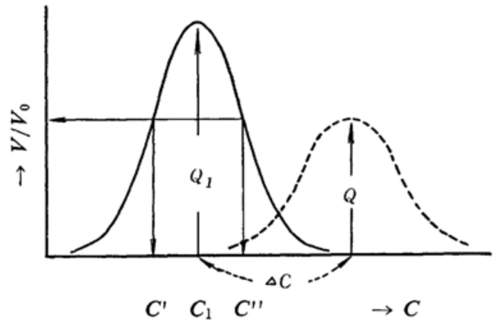

Fig. 2. These curves show the variation of coil character.

The coil shown in Fig. 3 is wound on the quartz bobbin (diameter 31 mm.) which has another quartz tube serving as a guide for the vessel containing the sample solution. The number of turns of the coil, which consists of a copper wire (diameter 1.3 mm.), is 17.5 and the height of the coil is 26 mm. The vessel for sample solution is also made of the quartz tube, of which the inner diameter is 17.1~3 mm. The length of the sample solution in the vessel is 65 mm. and its temperature is kept in the range of 25±0.5°C.

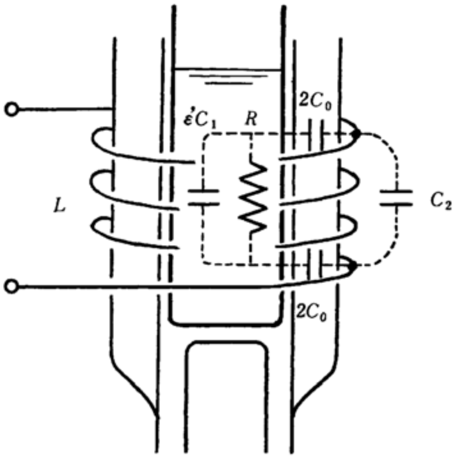

Fig. 3. Relationship between sample solution and coil, connected by equivalent circuit.

Calculation by Equivalent Circuit

The equivalent circuit of the coil containing the sample solution is considered as Fig. 3 (except the effect of eddy current), where ε' and R show the real part of the dielectric constant and the resistance of sample solution at high frequency (3 Mc.), respectively. The distributed capacity of the coil consists of capacities, C_0, C_1 and C_2. The notations of R and C_0 have the same physical meaning as that in Refs. 25, 29 and 28. The sample solution in the coil has the capacitance, which is omitted in Refs. 25 and 29, under the assumption that the effect of capacitance is negligible when the value of the resistance (R) is not so great. However, at the end of Ref. 29 "the dielectric constant of sample solution may be a significant factor" has been suggested. In the present paper the capacitance is expressed by the notation $\varepsilon' C_1$ in Fig. 3, since $\varepsilon' C_1$ as well as C_2 has been described in Ref. 28. Then the equivalent circuit of the total system is

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[28] S. Toyoda, This Bulletin, 33, 504 (1960).

[29] M. Honda, K. Nakano and A. Satsuka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 75, 1299 (1954).

[30] W. J. Blaedel et al., *Anal. Chem.*, 24, 198 (1952).

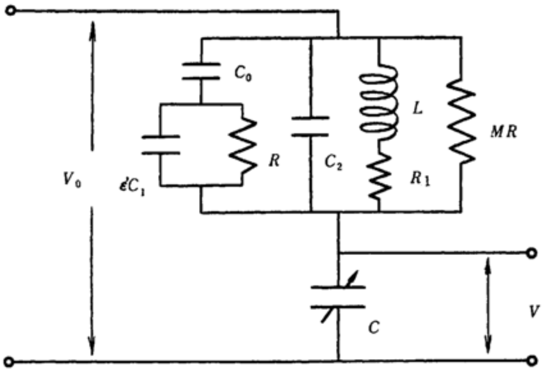

Fig. 4. Equivalent circuit of total system.

illustrated in Fig. 4, taking account of the eddy current in the sample solution and the loss of coil without sample solution (R_1). The resistance factor, MR, displays the effect of eddy current and has the same significance as KLR in Refs. 25, 29 and 28. The low resistance, R_1, will be calculated from the Q-value of the coil without sample solution. The position of R_1 in Fig. 4 is based on Fig. 8 in Ref. 28.

Thus the equations about Q and C at the tuning point are obtained by the following calculation. If Z_2 is the impedance of condenser C and Z_1 is the impedance of the rest in Fig. 4, Q and Z_1 are written as follows:

$$Q=\left|\frac{Z_2}{Z_1+Z_2}\right| \tag{1}$$

$$\begin{aligned}\frac{1}{Z_1}=&\frac{(\omega C_0)^2R}{1+\omega^2(\varepsilon' C_1+C_0)^2R^2}+\frac{R_1}{R_1{}^2+(\omega L)^2}\\&+\frac{1}{MR}+\boldsymbol{j}\left[\frac{\omega C_0\{1+\omega^2\varepsilon' C_1(\varepsilon' C_1+C_0)R^2\}}{1+\omega^2(\varepsilon' C_1+C_0)^2R^2}\right.\\&\left.+\omega C_2-\frac{\omega L}{R_1{}^2+(\omega L)^2}\right]\equiv A+\boldsymbol{j}B\end{aligned} \tag{2}$$

On the other hand, the variable condenser is adjusted at the tuning point under the constant frequency of oscillation. This means the following relation, as shown in Ref. 29.

$$(Z_1+Z_2)_{\text{imag}}=0 \tag{3}$$

After rearrangement, it is written as

$$-B\omega C=A^2+B^2 \tag{4}$$

Substituting the above equations into Eq. 1, the following relation is easily obtained.

$$Q=-\frac{B}{A} \tag{5}$$

If the Q of the coil without sample solution is denoted by Q_1, one obtains the following expression, substituting the condition ($\varepsilon'=1$, $R=\infty$) into Eq. 5:

$$Q_1=\frac{\omega L}{R_1}\left[1-\omega^2L\left(C_2+\frac{C_0C_1}{C_1+C_0}\right)\left\{1+\left(\frac{R_1}{\omega L}\right)^2\right\}\right] \tag{6}$$

Calculation of Distributed Capacity

The tuning capacity is shown by Eq. 4. After rearrangement, Eq. 4 is written as

$$\begin{aligned}&\left[1-\omega^2L\left(C_2+C_0\frac{1+qx^2}{1+x^2}\right)\left\{1+\left(\frac{R_1}{\omega L}\right)^2\right\}\right]\omega^2LC\\&=1-2\omega^2L\left(C_2+C_0\frac{1+qx^2}{1+x^2}\right)\\&\quad+\left\{\omega^2L\left(C_2+C_0\frac{1+qx^2}{1+x^2}\right)\right\}^2\left\{1+\left(\frac{R_1}{\omega L}\right)^2\right\}\\&\quad+\alpha^2\left\{\left(\frac{px}{1+x^2}\right)^2+\frac{1}{(Mpx)^2}\right\}\left\{1+\left(\frac{R_1}{\omega L}\right)^2\right\}\\&\quad+\frac{2\alpha px}{1+x^2}\frac{R_1}{\omega L}+\frac{2\alpha^2}{M(1+x^2)}\left\{1+\left(\frac{R_1}{\omega L}\right)^2\right\}\\&\quad+\frac{2\alpha}{pMx}\frac{R_1}{\omega L}\end{aligned} \tag{7}$$

where

$$x\equiv\omega(\varepsilon' C_1+C_0)R, \qquad \alpha\equiv\omega^2LC_0$$

$$p\equiv\frac{C_0}{\varepsilon' C_1+C_0} \qquad q\equiv\frac{\varepsilon' C_1}{\varepsilon' C_1+C_0}$$

Let us take the special case when the vessel in the coil has no sample solution, so that the tuning capacity for the coil without sample solution, C_l, is written as the following expression, substituting the condition ($\varepsilon'=1$, $x=\infty$) into the above equation.

$$\begin{aligned}&\left[1-\omega^2L\left(C_2+\frac{C_0C_1}{C_1+C_0}\right)\left\{1+\left(\frac{R_1}{\omega L}\right)^2\right\}\right]\omega^2LC_l\\&=1-2\omega^2L\left(C_2+\frac{C_0C_1}{C_1+C_0}\right)\\&\quad+\left\{\omega^2L\left(C_2+\frac{C_0C_1}{C_1+C_0}\right)\right\}^2\left\{1+\left(\frac{R_1}{\omega L}\right)^2\right\}\end{aligned} \tag{8}$$

On the other hand, C_0, C_1 are the order of magnitude 10^{-12} Farad or less and C_2 seems to be probably the same order, though C_2 may be larger than C_0 or C_1, and $M\approx10^3$, as being deduced from Refs. 25 and 28. As these capacities are much smaller in value than C_l (346×10^{-12} Farad), one obtains the following relation from Eq. 6.

$$Q_1\doteqdot\frac{\omega L}{R_1} \tag{9}$$

Thus, taking account of $Q_1\gg1$ (refer to Table II), Eq. 8 is written as follows:

$$C_l=\frac{1}{\omega^2L}-C_2-\frac{C_0C_1}{C_1+C_0} \tag{10}$$

Neglecting the second and the third terms, the inductance of the coil at 3 Mc. can be calculated ($L=8.1_4\times10^{-6}$ Henry), so that the loss of the coil is $0.80_3\,\Omega$ by Eq. 9 using $Q_1=191$ (mean value in Table II). If the resistance of the

TABLE I

Sample solution		25°C			Calcd.	Exp. (mean value)		f_1	f_2
		10^6	10^7	3×10^6	ΔC	ΔC	$\Delta C'$		
Carbon tetrachloride	ε'	2.17	2.17	2.17	-0.026	-0.03	-0.08	*810	*37000
	r	$>2\times10^{10}$	$>4\times10^8$	$>4\times10^8$					
n-Butyl alcohol	ε'	17.4	17.4	17.4	-0.215	-0.23	-0.28	3895	—
	r	1.1×10^7	4.3×10^5	$>4\times10^5$					
Ethyl alcohol	ε'	24.5	24.1	24.3	-0.258	-0.26	-0.31	4760	178000
	r	8.2×10^5	2.3×10^5	5×10^5					
Methyl alcohol	ε'	31	31	31	—	-0.29	-0.34	5560	189000
	r	2.9×10^5	2.2×10^5	2.5×10^5					
Nitrobenzene	ε'	35.6	34.4	35.2	-0.305	-0.31	-0.36	5720	192000
	r	6.3×10^6	5.8×10^5	6×10^5					
Distilled water	ε'	78.2	78.2	78.2	—	-0.39	-0.44	7880	210000
	r	5.8×10^5	5.0×10^5	5.5×10^5					

* Benzene.
Specific resistance unit, Ω·cm.; capacity unit, 10^{-12} Farad; frequency unit, cycle.

sample solution at high frequency is very great, in other words $x \gg 1$, all terms following the third term in the right-hand side of Eq. 7 can be neglected in comparison with the rest. Thus, one obtains

$$C=\frac{1}{\omega^2 L}-C_2-C_0\frac{1+qx^2}{1+x^2} \qquad (11)$$

In Fig. 2, the curve of V/V_0 vs. C changes as shown by the dotted line, after the sample solution is inserted into the coil. Then the following equation shows the difference, ΔC, between the tuning capacity of the two cases ($x=\infty$ and $x \gg 1$).

$$C-C_l=\frac{C_0 C_1}{C_1+C_0}-C_0\frac{1+qx^2}{1+x^2} \qquad (12)$$

In Table I, the values of specific resistance of organic solutions and distilled water at 10^6-, 10^7-cycles are calculated by the following relation,

$$\frac{1}{\rho}=\frac{f(\varepsilon'/\varepsilon_0)\tan\delta}{1.8\times10^{12}}\,[\text{mho-cm.}]\quad (f \text{ in c.p.s.})$$

as described in the literature[31], and the value of their dielectric constants is also detailed in Ref. 31. The values of dielectric constant and specific resistance at 3×10^6-cycle are deduced from the respective values at 10^6-, 10^7-cycles. The specific resistance of sample solution, r, is proportional to R.

$$R=kr \qquad (13)$$

On the other hand, the experimental values of ΔC and $\Delta C'$ in Table I are obtained by the following manipulation at 3 Mc. In the first place, one measures the tuning capacity for the coil, into which the quartz vessel containing the sample solution is inserted, by the method which was detailed previously. Again, the tuning capacity for the coil without the quartz vessel is measured by the same method. Thus the change of the tuning capacity, $\Delta C'$, which is caused by the vessel containing the sample solution, is obtained by subtracting the latter from the former. Similarly $\Delta C''(=-0.05\,\mu\mu$ Farad), which is caused by the quartz vessel without sample solution, is also obtained. Finally, ΔC is computed by subtracting $\Delta C''$ from $\Delta C'$.

Now, let us calculate the values of C_0 and C_1 using the methyl alcohol and the distilled water as sample solutions. The following equation can be introduced from Eq. 12,

$$C-C_l=\frac{C_1 C_0}{C_1+C_0}-\frac{\varepsilon' C_1 C_0}{\varepsilon' C_1+C_0} \qquad (14)$$

assuming the relations, $\omega^2\varepsilon' C_1(\varepsilon' C_1+C_0)R^2 \gg 1$, $\omega^2(\varepsilon' C_1+C_0)^2 R^2 \gg 1$ which may be considered to be correct since the value of their specific resistance is very large in Table I. Accordingly the simultaneous equation for two samples is obtained and one can find the results $C_0=0.52_3\times10^{-12}$, $C_1=0.025_3\times10^{-12}$ Farad. The capacity C_2 is neglected in the following discussions since the value can not be obtained by this method, to one's regret.

Calculation of *Q*-change and *M* Using Aqueous Solution

It has been described in Ref. 29 that the Q of coil containing the aqueous solution of hydrogen chloride changes with the concentration. The same results as this are obtained as shown in Table II and Fig. 5, when the quartz vessel containing the aqueous solution of potassium chloride or hydrogen chloride is placed in the coil. The values of Q_1 in Table II are the Q of coil without the quartz vessel. They are used instead of the Q-value of coil with only the quartz vessel, since the variation

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[31] Arthur R. von Hippel, "Dielectric Materials and Applications", The Technology Press of M. I. T. and J. Wiley & Sons, Inc., New York, Chapman & Hall, Ltd., London (1954), pp. 294, 361, 362, 364.

TABLE II

Aq. soln., N		r(Ω·cm., 25±0.5°C) cycle		Q_1	Q	$Q/Q_1\times100$	Mean value	
KCl	HCl	3×10^6	10^3				$Q/Q_1\times100$	$\varDelta C'$(pF)
(Dist. water)		*5.5×10^5 1 〃	$\sim10^6$	190.5 190	190 190.5	99.7 〃	99.7	−0.44
10^{-5}		3.3×10^4	2×10^5	190.5	190	99.7	99.7	−0.43
	10^{-5}	1.3 〃	10^5	191 〃	189 〃	99.0 〃	99.0	−0.43
10^{-4}		1.2 〃	4.2×10^4	192.5 〃	189.5 190	98.4 98.7	98.5	−0.44
	10^{-4}	6500	2.9 〃	192 192.5	189 〃	98.4 98.2	98.3	−0.44
3×10^{-4}		5070	2.2 〃	191 191.5	187 〃	97.9 97.7	97.8	−0.46
10^{-3}		3630	6600	192.5 192	186 185	96.6 96.3	96.5	−0.49
	10^{-3}	1680	2140	192 192.5	186.5 〃	97.1 96.9	97.0	−0.52
3×10^{-3}		1620	2280	192 〃	186.5 187	97.1 97.4	97.3	−0.54
0.01		454	**707	193 194	188 190	97.4 97.9	97.7	−0.54
0.03		220	244	188 189	185 〃	98.4 97.8	98.1	−0.56
	0.01	187	205	191 191.5	186 187	97.4 97.7	97.5	−0.55
0.1		31.3	**77.6	192.5 〃	183.5 183	95.3 95.1	95.2	−0.55
0.3		17.5	27.8	192.5 193	176 175.5	91.4 90.9	91.2	−0.61
	0.1	14.0	21.6	192 192.5	172.5 〃	89.8 89.6	89.7	−0.61
1		8.06	**8.94	192.5 〃	159 〃	82.6 〃	82.6	−0.76
3		3.34	3.40	190	132	69.5	69.5	−0.94
	1	2.75	2.62	190 189	127 126.5	66.8 67.0	66.9	−0.97

* Table I.
** Ref. 32.

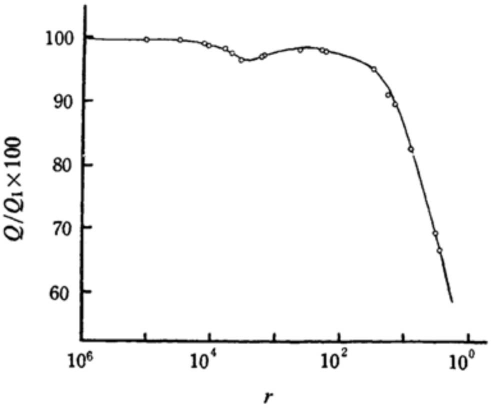

Fig. 5. Relationship between Q/Q_1 and specific resistance of aqueous solution.

of Q caused by the vessel is so small that one can not detect it. The value of Q_1 in Table II changes slightly in spite of an experiment made with the voltage stabilizer. And so the factor, Q/Q_1, will be picked up in the following discussion instead of considering the variation of Q. After rearrangement of Eq. 5, one obtains

$$\frac{Q}{Q_1}=\frac{1-\omega^2L\left\{C_2+\dfrac{C_0(1+qx^2)}{1+x^2}\right\}\left\{1+\left(\dfrac{R_1}{\omega L}\right)^2\right\}}{1-\omega^2L\left(C_2+\dfrac{C_0C_1}{C_1+C_0}\right)\left\{1+\left(\dfrac{R_1}{\omega L}\right)^2\right\}}\times\frac{1}{1+\alpha\left(\dfrac{px}{1+x^2}+\dfrac{1}{pMx}\right)\dfrac{\omega L}{R_1}\left\{1+\left(\dfrac{R_1}{\omega L}\right)^2\right\}} \tag{15}$$

The first term in the right-hand side is approximately equal to unity, taking account of the facts that the distributed capacity is much

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32) Compiled by Chem. Soc. Japan, "Handbook on Chemistry (Kagaku Benran)", Maruzen, Tokyo (1953), p. 603.

TABLE III

r	$\left(\frac{Q_1}{Q}-1\right)\frac{R_1}{\omega^2L^2}$	R	$\frac{(\omega C_0)^2R}{1+\omega^2(\varepsilon' C_1+C_0)^2R^2}$	MR	M	M'
2.75	1.69×10^{-5}	16.0	1.6×10^{-9}	5.92×10^4	3.70×10^3	7.01×10^3
3.34	1.50 〃	19.5	1.9 〃	6.67 〃	3.42 〃	6.12 〃
8.06	7.19×10^{-6}	47.1	4.6 〃	1.39×10^5	2.95 〃	4.83 〃
14.0	3.92 〃	81.7	7.9 〃	2.56 〃	3.13 〃	3.73 〃
17.5	3.29 〃	102	9.9 〃	3.05 〃	2.99 〃	3.49 〃
31.3	1.72 〃	183	1.8×10^{-8}	5.88 〃	3.21 〃	2.42 〃

$M_{\text{mean}}=3.2\times10^3$

smaller than C_l and $(R_1/\omega L)^2\ll1$. Therefore, the behavior of the curve of Q/Q_1 is chiefly ruled by the following function of ε', R or x

$$f(x)=\alpha\left(\frac{px}{1+x^2}+\frac{1}{pMx}\right)\frac{\omega L}{R_1} \tag{16}$$

Taking it into account that the dielectric constant of aqueous solution does not change greatly with concentration, since it has been shown in Refs. 30 and 33, one differentiates the function with respect to x and puts the differential coefficient equal to zero, so that the following conditions, which give the minimum and the maximum points of Q/Q_1 curve, are obtained:

$$x=\sqrt{\frac{p^2M-2\pm\sqrt{(p^2M-2)^2-4(p^2M+1)}}{2(p^2M+1)}} \tag{17}$$

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

On the other hand, the specific resistance, r, at 3×10^6-cycle shown in Table II is obtained by the following method. One connects the sample solution, which is contained in the proper glass pipe having the electrode of wire, parallel to the variable condenser of Q-meter and measures the Q-value, so that the next relation can be used:

$$r=\frac{1}{\omega C}\,\frac{QQ_1}{Q_1-Q}\,\frac{\sigma}{h} \tag{18}$$

where σ is the section area of sample solution and h the length of the one between two electrodes.

Let us consider the minimum point of Q/Q_1 curve. Assuming $p^2M\gg1$, the condition giving the minimum value is written as follows:

$$\omega(\varepsilon' C_1+C_0)R=1 \tag{19}$$

The concentration of aqueous solution giving minimum point seems to be 10^{-3} N of potassium chloride in Table II. The resistance of aqueous solution is proportional to the specific resistance of the one. Then one finds $K=5.84$, $(Q/Q_1)_{\min}=97.1\%$ by some calculations. The value of $(Q/Q_1)_{\min}$ is approximately in accordance with the experimental value. However, one should be contented with such consistency taking account of the fluctuation in the cases when measuring capacity, Q-value and so forth. The value of M can be calculated by the following expression.

$$\frac{1}{MR}=\left(\frac{Q_1}{Q}-1\right)\frac{R_1}{(\omega L)^2}-\frac{(\omega C_0)^2R}{1+\omega^2(\varepsilon' C_1+C_0)^2R^2} \tag{20}$$

In Table III, M' means the M-value obtained by calculation with the specific resistance of aqueous solution at 10^3-cycle instead of 3×10^6-cycle, so that the values of M' are rather scattered.

As a result of calculation about maximum point, one obtains $(Q/Q_1)_{\max}=99.0\%$, with the following equation taking account of $p^2M\approx100$.

$$\left(\frac{Q}{Q_1}\right)_{\max}\doteqdot\frac{1}{1+\dfrac{2\alpha Q_1\{1-(1/2p^2M)\}}{\sqrt{M}}} \tag{21}$$

This value seems to be near the value of Q/Q_1 for the aqueous solution of 3×10^{-2} N potassium chloride, though the correct experimental value of $(Q/Q_1)_{\max}$ is not evident. Now let us calculate the specific resistance of aqueous solution at maximum point, which is obtained by Eq. 17. Then, one finds it to be 307 Ω cm., which is located between the values for 10^{-2} N and 3×10^{-2} N of potassium chloride solutions. It may be considered that the maximum point is located in this interval. Though there are many assumptions on the process of calculation, they seem to become valid by some calculations using the value of ε', r, k and so forth.

In Ref. 28, some of the calculated values of depth at minimum point are considerably great or small 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. As a result of calculation taking another factor into account, it has been found that the consideration of the factor, $\varepsilon' C_1$, seems to be helpful for the solution of the problem. Similarly, the factor, $\varepsilon' C_1$, is

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33) W. J. Blaedel et al., *Anal. Chem.*, **24**, 1240 (1952).

also contained in the condition for the minimum point (Eq. 19). This factor has the same significant meaning as the one in Ref. 28, setting apart the point that a different value will be given to the proportional constant (k) in Eq. 13 due to $\varepsilon' C_1$, since Eq. 17 is slightly different from Eq. 20 in Ref. 29. When the dielectric constant of sample solution, ε', is very large as in the case of water, the term, $\varepsilon' C_1$, becomes greater than C_0. Therefore, the former can not be neglected in comparison with the latter, though C_1 is fairly small in comparison with C_0 in the present paper. The function $f(x)$, which determines the value of Q/Q_1 at minimum point, contains the factor p. Furthermore the value of this factor becomes somewhat smaller than unity and it depends upon the ratio of C_0 to $\varepsilon' C_1$, so that $(Q/Q_1)_{\min}$ is ruled to a great extent by this ratio. Then this result seems to support the previous view in Ref. 28.

TABLE IV

ε'	p	x at min.	x at max.	$(Q/Q_1)_{\min}$	p^2M
1	0.954	0.999	0.0185	87.9	2911
2	0.912	〃	0.0194	88.3	2660
3	0.873	〃	0.0202	88.8	2440
4	0.838	〃	0.0211	89.2	2246
5	0.805	〃	0.0219	89.6	2075
6	0.775	〃	0.0227	89.9	1940
7	0.747	〃	0.0236	90.3	1786
8	0.721	〃	0.0245	90.6	1663
9	0.697	〃	0.0254	90.9	1553
10	0.674	〃	0.0262	91.2	1453
20	0.508	0.998	0.0346	93.2	826.9
30	0.408	0.996	0.0432	94.5	532.8
40	0.341	0.994	0.0518	95.4	371.5
50	0.293	0.992	0.0603	95.9	273.8
60	0.256	0.990	0.0690	96.6	210.0
70	0.228	0.988	0.0775	96.8	166.2
80	0.205	0.985	0.0860	97.1	134.9
90	0.187	0.982	0.0946	97.3	111.5
100	0.171	0.980	0.103	97.5	93.88

It has been reported in Ref. 34 that "for high frequency titrations, changes of dielectric constant during the titration will be a factor in the determination of curve form only if there is an appreciable change in the composition of the solvent during the course of the titration". In the present paper, one considers that the dielectric constant of aqueous solution does not change greatly with the concentration. The value of $(Q/Q_1)_{\min}$ obtained by Eq. 15, however, seems to become smaller when C_0 becomes larger or ε', C_1 smaller. Therefore, it is very significant to consider how the curve of Q/Q_1 vs. x changes when a sample solution has another constant value ε'. From Eq. 17 the value of x in the case when Q/Q_1 has a minimum value, is independent upon ε',

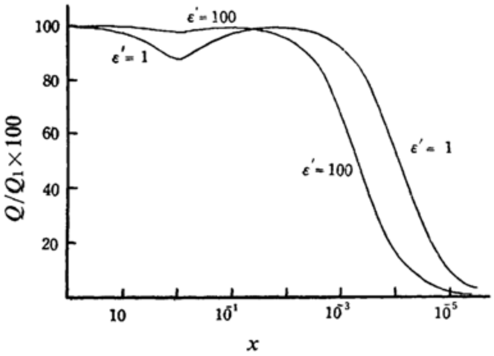

Fig. 6. Relation between values of Q/Q_1 for different dielectric constant.

TABLE V. VALUES OF Q/Q_1

ε'	x = 100	30	10	3	1	0.3	0.1	3×10^{-2}
1	99.7	99.1	97.4	92.3	87.9	92.9	97.2	98.6
4	99.8	99.2	97.7	93.1	89.2	93.8	97.5	98.9
10	〃	99.4	98.1	94.5	91.2	94.8	97.9	〃
40	99.9	99.7	99.0	97.1	95.4	97.3	98.7	98.8
80	〃	99.8	99.4	98.2	97.1	98.2	98.9	98.4
100	〃	〃	99.5	98.5	97.5	98.5	99.0	98.1

ε'	x = 10^{-2}	3×10^{-3}	10^{-3}	3×10^{-4}	10^{-4}	3×10^{-5}	10^{-5}	3×10^{-6}
1	98.8	96.9	91.2	76.1	51.4	24.1	9.6	3.1
4	98.7	96.4	90.3	73.5	48.1	21.7	8.5	2.7
10	98.4	95.7	88.2	69.2	42.7	18.3	7.0	2.2
40	97.3	91.9	79.1	53.2	32.6	10.1	3.6	1.1
80	95.8	87.2	69.7	40.7	18.7	6.4	2.2	0.7
100	94.9	85.1	65.5	36.4	15.9	5.4	1.9	0.6

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34) J. L. Hall et al., ibid., 26, 1539 (1954).

whereas the minimum value of Q/Q_1 depends on it, since Eq. 16 has the factor p and $p^2M \gg 1$, as shown in Table IV. On the contrary, in the case of the maximum, the value of x depends upon ε', whereas the maximum value of Q/Q_1 is independent on it (refer to Eq. 21). The values of Q/Q_1 for various dielectric constants are listed in Table V, and the relation between some of them is illustrated by Fig. 6.

Calculation of Capacity Change for Various Solutions

The change of tuning capacity, ΔC, is caused by inserting the sample solution into the coil. When the dielectric loss of sample solution is fairly small in value, in other words, the specific resistance is very large in value, ΔC can easily be calculated by Eq. 14. Then it seems to be found that the result of calculations for some organic solutions is consistent with the experimental value in Table I. On the other hand, the significant result[35] has been obtained using the heterodyne type instrument, which is based upon the principle that the frequency of an oscillator changes with a change of composition of the core material of the tank circuit coil. The beat frequency changes induced by a number of organic compounds at 4 Mc. have been measured. Therefore, some of them (f_1) are shown in Table I. As compared with ΔC, the beat frequency change increases with the decrease of ΔC. Consequently, this beat frequency change seems to be owing to the dielectric constant of core material (ε'), because the change of the tuning capacity due to core material means the change of the reasonance frequency of coil. Furthermore, significant results[36] have been obtained by the instrument with some modification of tank circuit. The beat frequency change has been observed, which is caused by the sample in the capacitor cell. Then some of them f_2 are listed in Table I as well as f_1. The meaning of the variation of ΔC seems to become more obvious, taking account of the similarity of the equivalent circuits for the condenser-type electrode and the coil in Ref. 28, and considering the following matter in Ref. 30. The response of many organic solutions is inherently simpler than that of conducting systems, for all changes are essentially capacitive.

Finally, let us consider the change of tuning capacity for the aqueous solution. In Table II the value of $\Delta C'$, monotonously decreases with the decrease of resistance of aqueous solution. On the other hand, investigating each term in Eq. 7, the value of the last term in the right-hand side becomes 7.9×10^{-5} when $x=3\times10^{-4}$ ($r=1.09\,\Omega\cdot$cm.). The minimum observable capacity with Q-meter is 0.01 $\mu\mu$ Farad, and $C_l=346$ $\mu\mu$ Farad, so that $(\Delta C)_{\min}/C_l=2.9\times10^{-5}$. This result seems to suggest that the value of the last term in Eq. 7 can reach sufficient value to be measured, when x approaches 3×10^{-4}. All terms following the third term in the right-hand side of Eq. 7 have smaller values than 7.9×10^{-5}. Thus they seem to be out of the question in the range of x more than 3×10^{-4}. Then, Eq. 11 can be used instead of Eq. 7, for the tuning capacity of coil containing aqueous solution, and so Eq. 12 will be discussed. The change of tuning capacity, ΔC, by Eq. 12 monotonously decreases with the decreasing of x, assuming that ε' is constant. Therefore, the behavior of the curve of ΔC vs. x obtained by Eq. 12 corresponds with the behavior of the curve of ΔC vs. r. But the value of ΔC calculated by Eq. 12 is greater than the experimental value in the range of the thick solution. The coil, perhaps, has some floating capacity which is not shown in Fig. 4 since it has been connected with the Q-meter by a rather long lead. This capacity may be one of the causes of discrepancy.

Conclusion

In the present paper, a method was proposed for the calculation of the distributed capacity of a coil, and the capacity was calculated by using two liquids, though C_2 can not be obtained. With these values and the equations as mentioned above, the Q-value for the aqueous solution of various concentrations could be calculated. In the case of an organic solution having a large specific resistance, the calculated values of the changes of tuning capacity (ΔC) agree with the experimental values, and the dielectric constant, ε', seems to be the predominant cause of the effect for a coil. In Ref. 28 "the consideration of the factor, $\varepsilon'C_1$, is significant in order to solve the problem" was found only by calculation. In the present paper, similarly, as a result of some calculations including the factor, $\varepsilon'C_1$, as well as C_0, it is shown that the dielectric constant, ε', is likely to be a significant factor for the variation of Q, though the dielectric loss (or the specific resistance) is also important.

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[35] P. W. West et al., ibid., **22**, 469 (1950).

[36] O. A. Nance et al., ibid., **24**, 214 (1952).