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Theory and Observation of Dielectric Relaxations due to the Interfacial Polarization for Terlamellar Structure

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On the basis of electrostatic laws, a dielectric theory is developed to explain dielectric relaxations due to the interfacial polarization for terlamellar structure composed of three phases. It is proven that the derived formula is equivalent to that for a series combination of three lumped capacitance-conductance circuit models. Some dielectric observation was carried out on composite systems of distilled water, a Teflon film and potassium chloride solutions, the results being in quantitative conformity with the dielectric theory developed.

KEY WORDS: Terlamellar structure/ Dielectric Relaxation/ Electrical conductivity/ Interfacial polarization/ Maxwell-Wagner relaxation/ permittivity/ Teflon film/

I. INTRODUCTION

In order to understand the characteristics of membranes of practical use such as filtration films, dialysis films, ultrafiltration membranes and reverse osmotic membranes, it is important to obtain information on those membranes in electrochemical equilibrium with the ambient aqueous solutions. Dielectric properties relevant to the ion permeation through the membranes are usually measured for the membranes sandwiched between two aqueous phases as shown in Fig. 5 later on.

This kind of membrane-aqueous phase system is assumed to be a series combination of three phases, each of which is represented routinely by a lumped capacitance-conductance (C-G) model as shown in Fig. 4. This model, however, should be subjected to justification in terms of electrostatic field quantities and laws applied to the composite dielectrics prior to the routine use of a lumped C-G model[1-8].

In the present work, a heterogeneous dielectric in terlamellar structure is formulated theoretically by means of electrostatic quantities and laws to show the dielectric relaxation behaviour. According to a consequent formula, the terlamellar structure will be seen to be equivalent to a series combination of the three lumped C-G models. Some experimental results of dielectric relaxation observed in the terlamellar dielectrics are shown to confirm the theoretical formulation.

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II. CONSTRUCTION OF THEORY ON THE BASIS OF ELECTROSTATIC FIELD LAWS

2.1 Fundamental Relations in the Quasi-electrostatic Field

A triphase system in terlamellar structure is depicted in Fig. 1, which is composed of Phase b (henceforth referred to with a subscript b), Phase f (subscript f) and Phase a (subscript a) inserted in a parallel-plate capacitor with unit area. Each electrode plate is charged with the electric charge Q_b or Q_a, respectively. The charge is assumed to accumulate on the boundary between Phases b and f, the charge density being denoted by σ_b. Similarly the charge is assumed to accumulate on the boundary between Phases f and a, the charge density being σ_a. Figure 1 includes electrostatic laws and expressions necessary for the explanation below, where vector quantities are assumed to have positive values for pointing to the right.

For a system with a uniformly charged infinite plane, electrostatics gives a succint relation that the contribution of the surface charge density to electric flux density, or electric displacement, outside the plane is equal to the surface charge density divided by two. Hence, the electrode charges Q_b, Q_a and the boundary charge densities σ_b, σ_a give rise to the constituent parts of the electric flux density, or the electric displacement, as shown in the lowest part of Fig. 1. The elctric flux densities D_b, D_f and D_a are thus represented as follows:

$$D_b = \frac{Q_b - Q_a}{2} - \frac{\sigma_b}{2} - \frac{\sigma_a}{2}. \tag{1}$$

$$D_f = \frac{Q_b - Q_a}{2} + \frac{\sigma_b}{2} - \frac{\sigma_a}{2}. \tag{2}$$

$$D_a = \frac{Q_b - Q_a}{2} + \frac{\sigma_b}{2} + \frac{\sigma_a}{2}. \tag{3}$$

The relation between the flux density D_b, D_f or D_a and the electric field E_b, E_f or E_a is given by

$$E_b = \frac{D_b}{\epsilon_v \varepsilon_b}, \quad E_f = \frac{D_f}{\epsilon_v \varepsilon_f}, \quad \text{and} \quad E_a = \frac{D_a}{\epsilon_v \varepsilon_a}, \tag{4}$$

respectively, where ε is the relative permittivity of the respective phase, and $\epsilon_v = 0.088542$ pF cm^{-1} is the permittivity of vacuum.

Potential differences V_b, V_f and V_a for respective phases are given by

$$V_b = E_b d_b, \quad V_f = E_f d_f, \quad \text{and} \quad V_a = E_a d_a \ , \tag{5}$$

where d_b, d_f or d_a denotes the thickness of the respective phases. The total potential difference V is the sum of V_b, V_f and V_a, that is,

$$V = V_b + V_f + V_a. \tag{6}$$

Using the electrical conductivities κ_b, κ_f and κ_a, the electric current densities i_b, i_f

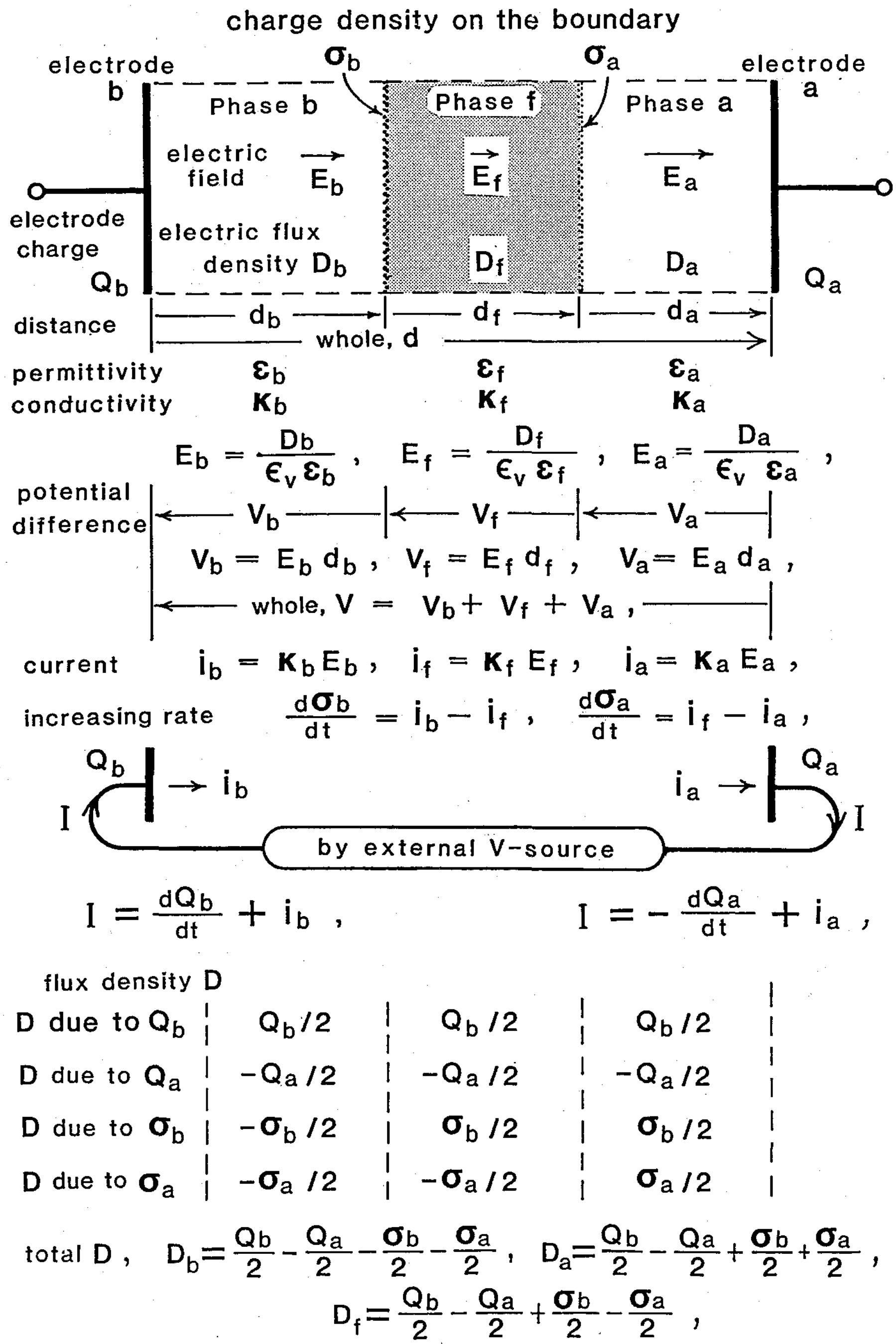


Fig. 1. Quasi-electrostatic fields, the related electric phenomena and the laws concerned for a terlamellar structure in a parallel-plate capacitor.

and i_a are given by

$$i_b = \kappa_b E_b, \qquad i_f = \kappa_f E_f, \qquad \text{and} \qquad i_a = \kappa_a E_a. \tag{7}$$

As regards the charge density σ_b per unit area on the boundary surface between Phase b and Phase f, its increasing rate $d\sigma_b/dt$ against time t is the difference of the current density i_b and i_f, that is,

$$\frac{d\sigma_b}{dt} = i_b - i_f. \tag{8}$$

In a similar manner, we have

$$\frac{d\sigma_a}{dt} = i_f - i_a. \tag{9}$$

The inflow current density I must be equal to the outflow current density owing to the total charge conservation law, being given by

$$\frac{dQ_b}{dt} + i_b = I = -\frac{dQ_a}{dt} + i_a. \tag{10}$$

From Eqs. 10, 8 and 9, we have

$$\frac{d}{dt}(Q_b + Q_a) = -i_b + i_a = -\frac{d}{dt}(\sigma_b + \sigma_a). \tag{11}$$

Integrating Eq. 11 with null integration constant corresponding to the neutral condition, we have

$$Q_b + Q_a = -(\sigma_b + \sigma_a). \tag{12}$$

The above are all of the expressions to describe the terlamellar system shown in Fig. 1.

For simplification of succeeding calculation, we put as follows:

$$\delta_b \equiv \frac{d_b}{\epsilon_v \varepsilon_b}, \qquad \delta_f \equiv \frac{d_f}{\epsilon_v \varepsilon_f}, \qquad \delta_a \equiv \frac{d_a}{\epsilon_v \varepsilon_a}, \tag{13}$$

$$k_b \equiv \frac{\kappa_b}{\epsilon_v \varepsilon_b}, \qquad k_f \equiv \frac{\kappa_f}{\epsilon_v \varepsilon_f}, \qquad k_a \equiv \frac{\kappa_a}{\epsilon_v \varepsilon_a}, \tag{14}$$

2.2 Guideline and Procedure of Successive Calculation

The course of successive calculation is apt to be in confusion because of too mamy formulas and too tedious rearrangement. The following items are pointed out to perform the calculation efficiently.

(i) In the present problem, independent variables are Q_b, Q_a, σ_b and σ_a in principle. Since Eqs. 1, 2 and 3 include a term $Q_b - Q_a$, the calculation can be simplified in practice to obtain three independent variables $Q_b - Q_a$, σ_b and σ_a. Hence we have to find three formulas which include the three variables only.

(ii) By eliminating $Q_b - Q_a$ among the three formulas obtained, two formulas are derived which include σ_b and σ_a only. The two formulas are to be simultaneous differential equations of the first order with respect to time t.

(iii) By eliminating σ_b among the two simultaneous differential equations of the first order, we derive a differential equation of the second order including σ_a only. By solving the second order differential equation, a solution of σ_a can be obtained.

(iv) A solution of σ_b can be derived by use of the solution of σ_a. Solutions of Q_b and Q_a are also obtained by use of σ_b and σ_a.

(v) Next, solutions of i_f, i_b and i_a are derived by use of Q_b, Q_a, σ_b and σ_a obtained above.

(vi) The inflow and outflow current density I is expressed with dQ_b/dt, i_b, dQ_a/dt and i_a. By use of the formulas of current density I, the apparent complex permittivity for the whole system can be expressed in terms of Q_b, i_b, Q_a and i_a.

(vii) The expressions of Q_b, Q_a, i_b and i_a obtained are introduced into the complex permittivity formula of the whole system derived above. After rearrangement an expression of the complex permittivity is written out to represent two dielectric relaxations.

(viii) In the course of rewriting and rearranging these expressions, some terms are expressed with a factor of $1/[1+j(\omega/\omega_P)]$ and $1/[1+j(\omega/\omega_Q)]$, which signify the dielectric relaxations. Further calculation with keeping this type of factors is very intricate and difficult to attain to the final expressions. An ingenious method of rearrangement is to make up a factor $1/[(j\omega+\omega_P)(j\omega+\omega_Q)]$, which is a synthesized form of the two factors: $1/[1+j(\omega/\omega_P)]$ and $1/[1+j(\omega/\omega_Q)]$. This particular technique of calculation makes further rearrangement much easier.

2.3 Replacement of various Expressions

For the sake of simplification in the course of cumbersome calculation, some replacements and the consequent simplified relations are summarized here.

$$S \equiv \delta_b + \delta_f + \delta_a, \tag{15}$$

$$R \equiv \frac{d_b}{\kappa_b} + \frac{d_f}{\kappa_f} + \frac{d_a}{\kappa_a}, \tag{16}$$

$$T_b \equiv \delta_b - \delta_f - \delta_a, \qquad T_a \equiv \delta_b + \delta_f - \delta_a, \tag{17}$$

$$J \equiv k_a + k_f, \qquad G \equiv k_b + k_f, \tag{18}$$

$$H \equiv k_b - k_f, \qquad K \equiv k_a - k_f, \tag{19}$$

$$L \equiv k_b(\delta_a + \delta_f) + k_f\delta_b, \qquad M \equiv k_a(\delta_b + \delta_f) + k_f\delta_a, \tag{20}$$

$$H - K = k_b - k_a = \frac{\kappa_b}{\epsilon_v \varepsilon_b} - \frac{\kappa_a}{\epsilon_v \varepsilon_a}, \tag{21}$$

$$A \equiv -\frac{L}{S}, \qquad B \equiv -\frac{H}{S}\delta_a, \qquad C \equiv \frac{H}{S}V, \tag{22}$$

$$D \equiv -\frac{K}{S}\delta_b, \qquad E \equiv -\frac{M}{S}, \qquad F \equiv -\frac{K}{S}V, \tag{23}$$

$$A + E = \frac{-1}{S}(L + M)$$

$$= \frac{-1}{S}[k_b(\delta_a + \delta_f) + k_a(\delta_b + \delta_f) + k_f(\delta_b + \delta_a)], \tag{24}$$

$$A - E = \frac{-1}{S}(L - M)$$

$$= \frac{-1}{S}[k_b(\delta_a + \delta_f) - k_a(\delta_b + \delta_f) + k_f(\delta_b - \delta_a)], \tag{25}$$

$$AE = \frac{LM}{S^2},$$

$$= \frac{1}{S^2}[k_b(\delta_a + \delta_f) + k_f\delta_b][k_a(\delta_b + \delta_f) + k_f\delta_a], \tag{26}$$

$$BD = \frac{HK}{S^2}\delta_b\delta_a = \frac{1}{S^2}\delta_b\delta_a(k_b - k_f)(k_a - k_f), \tag{27}$$

$$AE - BD = \frac{1}{S}(k_b k_a \delta_f + k_b k_f \delta_a + k_a k_f \delta_b), \tag{28}$$

$$AK + DH = -K k_b = -k_b(k_a - k_f), \tag{29}$$

$$BK + EH = -H k_a = -k_a(k_b - k_f), \tag{30}$$

$$(AK + DH) - (BK + EH) = k_f(\mathrm{H} - \mathrm{K}) = k_f(k_b - k_a), \tag{31}$$

$$AF = \frac{KL}{S^2}V = \frac{V}{S^2}[k_b(\delta_a + \delta_f) + k_f\delta_b](k_a - k_f), \tag{32}$$

$$DC = -\frac{HK}{S^2}V\delta_b = \frac{-V}{S^2}(k_b - k_f)(k_a - k_f)\delta_b, \tag{33}$$

$$AF - DC = \frac{V}{S}(k_a - k_f)k_b. \tag{34}$$

2.4 Derivation of three Expressions including three variables $Q_b - Q_a$, σ_b and σ_a

Substitution of Eqs. 5, 4, 1, 2, 3, 13, 15 and 17 in turn into Eq. 6 yields a new expression of V as follows:

$$V = V_b + V_f + V_a = E_b d_b + E_f d_f + E_a d_a,$$

$$= \frac{D_b}{\epsilon_v \varepsilon_b} d_b + \frac{D_f}{\epsilon_v \varepsilon_f} d_f + \frac{D_a}{\epsilon_v \varepsilon_a} d_a,$$

$$= \frac{S}{2}(Q_b - Q_a) - \frac{T_b}{2}\sigma_b - \frac{T_a}{2}\sigma_a. \tag{35}$$

Rearrangement of Eq. 35 with respect to $Q_b - Q_a$ gives

$$Q_b - Q_a = \frac{1}{S}(T_b\sigma_b + T_a\sigma_a + 2V). \tag{36}$$

In a similar manner, substitution of Eqs. 7, 4, 1, 2, 3, 18 and 19 in turn into Eq. 8 yields a new expression of $d\sigma_b/dt$ as follows:

$$\frac{d\sigma_b}{dt} = \frac{H}{2}(Q_b - Q_a) - \frac{G}{2}\sigma_b - \frac{H}{2}\sigma_a, \tag{37}$$

Substituting Eq. 36 for $Q_b - Q_a$ in Eq. 37 yields the following equation:

$$\frac{d\sigma_b}{dt} = -\frac{L}{S}\sigma_b - \frac{H}{S}\delta_a\sigma_a + \frac{H}{S}V. \tag{38}$$

Replacement in the above equation by Eq. 22 gives

$$\frac{d\sigma_b}{dt} = A\sigma_b + B\sigma_a + C. \tag{39}$$

In a similar manner, Eq. 9 is rearranged as

$$\frac{d\sigma_a}{dt} = -\frac{K}{S}\delta_b\sigma_b - \frac{M}{S}\sigma_a - \frac{K}{S}V. \tag{40}$$

Hence, replacement in the above equation by Eq. 23 gives

$$\frac{d\sigma_a}{dt} = D\sigma_b + E\sigma_a + F. \tag{41}$$

Here Items i and ii in subsection 2.2 have been dealed with.

2.5 Derivation and the Solution of the Second Order Differential Equation of σ_a

Eliminating σ_b-term between Eqs. 39 and 41, we have

$$-D\frac{d\sigma_b}{dt} = (AE - BD)\sigma_a + AF - DC - A\frac{d\sigma_a}{dt}. \tag{42}$$

Differentiating Eq. 41 with respect to t, we have

$$\frac{d^2\sigma_a}{dt^2} - D\frac{d\sigma_b}{dt} - E\frac{d\sigma_a}{dt} = \frac{dF}{dt}. \tag{43}$$

Substituting Eq. 42 for $Dd\sigma_b/dt$ in Eq. 43, we have the second order differential equation of σ_a as follows:

$$\frac{d^2\sigma_a}{dt^2} - (A+E)\frac{d\sigma_a}{dt} + (AE - BD)\sigma_a = DC - AF + \frac{dF}{dt}. \tag{44}$$

For the purpose of obtaining a general solution of Eq. 44, we consider the following linear homogeneous differential equation:

$$\frac{d^2\sigma_a}{dt^2} - (A+E)\frac{d\sigma_a}{dt} + (AE - BD)\sigma_a = 0, \tag{45}$$

which is the form with left side zero in Eq. 44. A general solution of this Eq. 45 is assumed to have the following form:

$$\sigma_a = \text{const} \times e^{mt}, \tag{46}$$

where m is a certain constant to be determined below.

Substituting Eq. 46 for σ_a in Eq. 45, we have

$$m^2 - (A+E)m + (AE - BD) = 0. \tag{47}$$

Two roots m_Q and m_P of this quadratic equation 47 are readily obtained. For the sake of convenience during the calculation, two quantities ω_Q and ω_P are introduced which are just opposite to m_Q and m_P in sign. Hence the expressions of ω_Q, ω_P, m_Q and m_P are given as follows:

$$\omega_Q \equiv -m_Q, \tag{48}$$

$$= \frac{1}{2}[-(A+E) + \sqrt{(A+E)^2 - 4(AE-BD)}] \tag{49}$$

$$= \frac{1}{2}[-(A+E) + \sqrt{(A-E)^2 + 4BD}], \tag{50}$$

$$\omega_P \equiv -m_P \tag{51}$$

$$= \frac{1}{2}[-(A+E) - \sqrt{(A+E)^2 - 4(AE-BD)}] \tag{52}$$

$$= \frac{1}{2}[-(A+E) - \sqrt{(A-E)^2 + 4BD}]. \tag{53}$$

Mutual situations among m_Q, m_P, ω_Q and ω_P are shown schematically in Fig. 2.

Using the relation between the roots and the coefficients of Eq. 47, we have

$$\omega_Q + \omega_P = -(m_Q + m_P)$$

$$= -(A+E) = \frac{1}{S}(L+M) \tag{54}$$

$$= \frac{1}{S}[k_b(\delta_a + \delta_f) + k_a(\delta_b + \delta_f) + k_f(\delta_b + \delta_a)] > 0, \tag{55}$$

$$\omega_Q \omega_P = m_A m_P = AE - BD \tag{56}$$

$$= \frac{1}{S}(k_b k_a \delta_f + k_b k_f \delta_a + k_a k_f \delta_b) > 0. \tag{57}$$

Therefore, we have always $\omega_Q > 0$ and $\omega_P > 0$. Hence the general solution of Eq. 45 is expressed as

$$\sigma_a = \text{const} \times e^{-\omega_Q t} + \text{const} \times e^{-\omega_P t}. \tag{58}$$

The boundary charge density σ_a of this Eq. 58 tends toward zero for $t \to \infty$, being negligibly small after sufficiently long time t.

Now a particular solution of Eq. 44 will be derived provided that an external a.c. voltage applied to the electrodes is expressed as

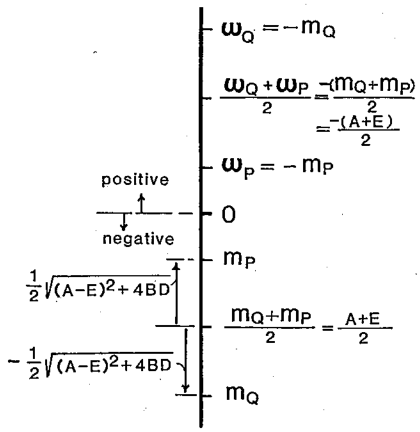


Fig. 2. Relative location among m_Q, m_P, ω_Q and ω_P in relation to the roots of Eq. 47.

$$V = V_0 e^{j\omega t}, \tag{59}$$

where V_0 is the amplitude of the a.c. voltage, $\omega = 2\pi \times$ frequency is the angular frequency, and $j = \sqrt{-1}$ is the imaginary unit. The quantities C and F given by Eqs. 22 and 23 also include the factor $e^{j\omega t}$. Hence σ_a given by Eq. 44 must have the following form:

$$\sigma_a = \sigma_{a0} e^{j\omega t}, \tag{60}$$

where σ_{a0} is the amplitude of σ_a.

Substituting Eq. 58 for σ_a in Eq. 44, we have

$$[(j\omega)^2 - (A+E)j\omega + (AE - BD)]\,\sigma_a = DC - AF + j\omega F. \tag{61}$$

Hence we have

$$\sigma_a = \frac{DC - AF + j\omega F}{(j\omega)^2 - (A+E)j\omega + (AE - BD)}. \tag{62}$$

Taking advantage of the previous analysis for the two roots m_Q and m_P in Eq. 47, we can rewrite the denominator of Eq. 62 as follows:

$$\sigma_a = \frac{DC - AF + j\omega F}{(j\omega - m_Q)(j\omega - m_P)} \tag{63}$$

$$= \frac{DC - AF + j\omega F}{(j\omega + \omega_Q)(j\omega + \omega_P)}, \tag{64}$$

Here Item iii in subsection 2.2 has been dealt with.

2.6 Derivation of Expressions for σ_b, σ_a, Q_b, Q_a, i_b, i_f and i_a

By use of Eqs. 22 and 23, Eq. 64 is rearranged as

$$\sigma_a = -\frac{j\omega K - (AK + DH)}{(j\omega + \omega_Q)(j\omega + \omega_P)} \cdot \frac{V}{S}. \tag{65}$$

Substituting Eq. 65 for σ_a in Eq. 41 and using $d/dt = j\omega$, we have

$$\sigma_b = \frac{j\omega H - (BK + EH)}{(j\omega + \omega_Q)(j\omega + \omega_P)} \cdot \frac{V}{S}. \tag{66}$$

By use of Eqs. 29, 30 and 19, Eqs. 66 and 65 are rearranged as

$$\sigma_b = \frac{k_b - k_f}{S} \cdot \frac{j\omega + k_a}{(j\omega + \omega_Q)(j\omega + \omega_P)} V, \tag{67}$$

$$\sigma_a = -\frac{k_a - k_f}{S} \cdot \frac{j\omega + k_b}{(j\omega + \omega_Q)(j\omega + \omega_P)} V, \tag{68}$$

For further rearrangement of formulas, we take notice of the following identities:

$$\left(\beta + \frac{1}{j\omega}\right)\frac{j\omega\gamma + \alpha}{(j\omega + \omega_Q)(j\omega + \omega_P)} = \frac{\alpha}{j\omega\omega_Q\omega_P} + \frac{j\omega(\beta\gamma\omega_Q\omega_P - \alpha) + \omega_Q\omega_P(\gamma + \beta\alpha) - (\omega_Q + \omega_P)\alpha}{\omega_Q\omega_P(j\omega + \omega_Q)(j\omega + \omega_P)}. \tag{69}$$

$$\frac{j\omega\beta + \alpha}{(j\omega + \omega_Q)(j\omega + \omega_P)} = \frac{1}{\omega_Q - \omega_P} \cdot \frac{\frac{\alpha}{\omega_P} - \beta}{1 + j\frac{\omega}{\omega_P}} + \frac{1}{\omega_Q - \omega_P} \cdot \frac{\beta - \frac{\alpha}{\omega_Q}}{1 + j\frac{\omega}{\omega_Q}}. \tag{70}$$

$$\frac{j\omega}{1 + j\frac{\omega}{\omega_0}} = \omega_0 - \frac{\omega_0}{1 + j\frac{\omega}{\omega_0}} = \omega_0\left(1 - \frac{1}{1 + j\frac{\omega}{\omega_0}}\right). \tag{71}$$

By use of Eq. 70, Eqs. 67 and 68 are rearranged to the expressions consisting of two relaxation terms as follows:

$$\sigma_b = \left[\frac{k_b - k_f}{S(\omega_Q - \omega_P)} \cdot \frac{\frac{k_a}{\omega_P} - 1}{1 + j\frac{\omega}{\omega_P}} + \frac{k_b - k_f}{S(\omega_Q - \omega_P)} \cdot \frac{1 - \frac{k_a}{\omega_Q}}{1 + j\frac{\omega}{\omega_Q}}\right] V. \tag{72}$$

$$\sigma_a = \left[-\frac{k_a - k_f}{S(\omega_Q - \omega_P)} \cdot \frac{\frac{k_b}{\omega_P} - 1}{1 + j\frac{\omega}{\omega_P}} - \frac{k_a - k_f}{S(\omega_Q - \omega_P)} \cdot \frac{1 - \frac{k_b}{\omega_Q}}{1 + j\frac{\omega}{\omega_Q}}\right] V. \tag{73}$$

The sum of Eqs. 67 and 68 is given by

$$\sigma_b + \sigma_a = \frac{k_b - k_a}{S} \cdot \frac{j\omega + k_f}{(j\omega + \omega_Q)(j\omega + \omega_P)} V. \tag{74}$$

By use of Eq. 70, Eq. 74 is rearranged to

$$\sigma_b + \sigma_a = \left[\frac{k_b - k_a}{S(\omega_Q - \omega_P)} \cdot \frac{\frac{k_f}{\omega_P} - 1}{1 + j\frac{\omega}{\omega_P}} + \frac{k_b - k_a}{S(\omega_Q - \omega_P)} \cdot \frac{1 - \frac{k_f}{\omega_Q}}{1 + j\frac{\omega}{\omega_Q}} \right] V. \tag{75}$$

The expressions of Q_b and Q_a are derived by addition or substraction of Eqs. 12 and 36 by aid of Eq. 17 as follows:

$$Q_b = \frac{1}{S}[- (\delta_a + \delta_f)\sigma_b - \delta_a\sigma_a + V]. \tag{76}$$

$$Q_a = \frac{1}{S}[- \delta_b\sigma_b - (\delta_b + \delta_f)\sigma_a - V]. \tag{77}$$

Substitution of Eqs. 4, 1, 2, 3 and 36 into Eq. 7 leads to the following expressions for i_f, i_b and i_a:

$$i_f = \frac{1}{S}k_f(\delta_b\sigma_b - \delta_a\sigma_a + V), \tag{78}$$

$$i_b = \frac{1}{S}k_b[- (\delta_a + \delta_f)\sigma_b - \delta_a\sigma_a + V] = k_bQ_b, \tag{79}$$

$$i_a = \frac{1}{S}k_a[\delta_b\sigma_b + (\delta_b + \delta_f)\sigma_a + V] = - k_aQ_a. \tag{80}$$

Here, we have completed Items iv and v in subsection 2.2.

2.7 Derivation and Calculation of the Complex Permittivity Formula for the Apparent Capacitor System

In order to derive the complex permittivity formula for the capacitor, attention is paid to a connection between the capacitor and the exterior circuit shown in Fig. 3. If we use the current density I which is defined and used in Fig. 1, the total current in Fig. 3 is given by $I\cdot\Gamma$, where Γ is the electrode surface area. The total current $I\cdot\Gamma$ is represented by the voltage V multiplied by the complex conductance $\mathbf{G}^*$, that is,

$$I\cdot\Gamma = VG^*. \tag{81}$$

The complex conductance $\mathbf{G}^*$ is given by

$$G^* = j\omega C^* = j\omega\varepsilon^*\epsilon_v\frac{\Gamma}{d}, \tag{82}$$

where $\mathbf{C}^*$ is the complex capacitance, $\omega = 2\pi f$ the angular frequency of the a.c. voltage applied, $\varepsilon^* = \varepsilon + \kappa/(j\omega\epsilon_v)$ the complex relative permittivity of the composite capacitor, and d is the separation or distance of the two electrodes.

By use of Eqs. 82, 81, 10, and $d/dt = j\omega$, the expression of ε^*/d is rearranged as follows:

$$\frac{\varepsilon^*}{d} = \frac{G^*}{j\omega \in_v \Gamma} = \frac{I}{j\omega \in_v V} \tag{83}$$

$$= \frac{-j\omega Q_a + i_a}{j\omega \in_v V} = \frac{-Q_a}{\in_v V} + \frac{i_a}{j\omega \in_v V} \tag{84}$$

$$= \frac{j\omega Q_b + i_b}{j\omega \in_v V} = \frac{Q_b}{\in_v V} + \frac{i_b}{j\omega \in_v V} \quad . \tag{85}$$

Substituting Eq. 76 for Q_b and Eq. 79 for i_b in Eq. 85 yields the following formula.

$$\frac{\varepsilon^*}{d} = \frac{1}{\in_v S} + \frac{k_b}{j\omega \in_v S} + \frac{k_b}{\in_v SV}\left(\frac{1}{k_b} + \frac{1}{j\omega}\right)[-\delta_f \sigma_b - \delta_a(\sigma_b + \sigma_a)]. \tag{86}$$

Substituting Eq. 67 for σ_b and Eq. 74 for $\sigma_b + \sigma_a$ in Eq. 86, we have the following formula after tiresome rearrangement:

$$\frac{\varepsilon^*}{d} = \frac{1}{\in_v S} + \frac{k_b}{j\omega \in_v S} + \frac{k_b}{\in_v S^2}\left(\frac{1}{k_b} + \frac{1}{j\omega}\right)\frac{j\omega\eta + \zeta}{(j\omega + \omega_Q)(j\omega + \omega_P)}, \tag{87}$$

where

$$\eta = -(k_b - k_a)\delta_a - (k_b - k_f)\delta_f, \tag{88}$$

$$\zeta = -k_a(k_b - k_f)\delta_f - k_f(k_b - k_a)\delta_a. \tag{89}$$

Now the rearrangement of Eq. 87 will proceed to the function form with relaxation terms.

By use of Eq. 69, the third term of the right side of Eq. 87 is rearranged as follows:

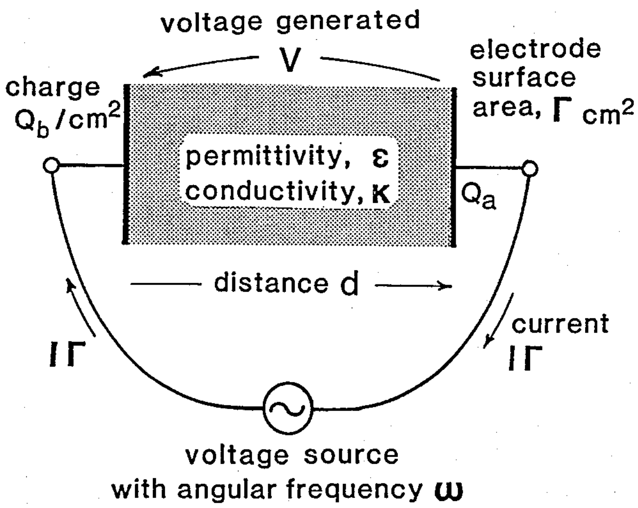


Fig. 3. Explanation of a complex permittivity for the whole of the triphase system in terms of the outside arrangements.

$$\frac{\varepsilon^*}{d}=\frac{1}{\in_v S}+\frac{k_b}{j\omega\in_v S}$$

$$+\frac{k_b}{\in_v S^2}\left[\frac{\zeta}{j\omega\omega_Q\omega_P}+\frac{j\omega\left(\frac{\omega_Q\omega_P}{k_b}\eta-\zeta\right)+\omega_Q\omega_P\left(\eta+\frac{\zeta}{k_b}\right)-(\omega_Q+\omega_P)\zeta}{\omega_Q\omega_P(j\omega+\omega_Q)(j\omega+\omega_P)}\right] \tag{90}$$

$$=\frac{1}{\in_v S}+\frac{k_b}{j\omega\in_v S}+\frac{k_b\zeta}{j\omega SS\omega_Q\omega_P}$$

$$+\frac{k_b}{\in_v S^2\omega_Q\omega_P}\cdot\frac{j\omega\left(\frac{\omega_Q\omega_P}{k_b}\eta-\zeta\right)+\omega_Q\omega_P\left(\eta+\frac{\zeta}{k_b}\right)-(\omega_Q+\omega_P)\zeta}{(j\omega+\omega_Q)(j\omega+\omega_P)}. \tag{91}$$

The sum of the second and the third terms of Eq. 91 is

$$\text{the sum}=\frac{1}{j\omega\in_v}\cdot\frac{1}{\frac{d_b}{\kappa_b}+\frac{d_f}{\kappa_f}+\frac{d_a}{\kappa_a}}=\frac{1}{j\omega\in_v R}, \tag{92}$$

where

$$\mathrm{R}\equiv\frac{d_b}{\kappa_b}+\frac{d_f}{\kappa_f}+\frac{d_a}{\kappa_a}. \tag{93}$$

Thus Eq. 91 is simplified to

$$\frac{\varepsilon^*}{d}=\frac{1}{\in_v S}+\frac{1}{j\omega\in_v R}$$

$$+\frac{j\omega(\omega_Q\omega_P\eta-k_b\zeta)+\omega_Q\omega_P(k_b\eta+\zeta)-(\omega_Q+\omega_P)k_b\zeta}{\in_v S^2\omega_Q\omega_P(j\omega+\omega_Q)(j\omega+\omega_P)}, \tag{94}$$

Each term in the numerator of the third term of the right side of Eq. 94 is rearranged respectively to

$$j\omega(\omega_Q\omega_P\eta-k_b\zeta)$$

$$=j\omega\frac{1}{S}[(k_b-k_a)^2k_f\delta_b\delta_a+(k_b-k_f)^2k_a\delta_b\delta_f+(k_a-k_f)^2k_b\delta_a\delta_f], \tag{95}$$

$$\equiv j\omega\Phi.$$

$$\omega_Q\omega_P(k_b\eta+\zeta)-(\omega_Q+\omega_P)k_b\zeta$$

$$=\frac{1}{S}[(k_b-k_a)^2k_f^2\delta_b\delta_a+(k_b-k_f)^2k_a^2\delta_b\delta_f+(k_a-k_f)^2k_b^2\delta_a\delta_f]. \tag{96}$$

$$\equiv\Lambda.$$

Thus Items vi and vii in subsection 2.2 are all completed.

In a similar manner, Eq. 84 yields the same expression as Eq. 94, if Eq. 77 for Q_a and Eq. 80 for i_a are substituted in Eq. 84.

2.8 Concluding Summary of the Theoretical Development based on Electrostatic Field Laws

The expressions derived and the associated conclusion are summarized as follows:

From Eq. 94, the complex relative permittivity ε^* for the whole system in terlamellar structure is given by

$$\varepsilon^* = \frac{d}{\epsilon_v S} + \frac{d}{\epsilon_v S^2 \omega_Q \omega_P} \cdot \frac{j\omega\Phi + \Lambda}{(j\omega + \omega_Q)(j\omega + \omega_P)} + \frac{d}{j\omega \epsilon_v R}. \tag{97}$$

Alternatively, by use of Eq. 70, Eq. 97 is rearranged as

$$\varepsilon^* = \frac{d}{\epsilon_v S} + \frac{d}{\epsilon_v S^2 \omega_Q \omega_P (\omega_Q - \omega_P)} \left[\frac{\frac{\Lambda}{\omega_P} - \Phi}{1 + j\frac{\omega}{\omega_P}} + \frac{\Phi - \frac{\Lambda}{\omega_Q}}{1 + j\frac{\omega}{\omega_Q}} \right]$$
$$+ \frac{d}{j\omega \epsilon_v R}. \tag{98}$$

In the right side of this Eq. 98, the first term means the limiting permittivity at high frequencies, d/R in the third term giving the limiting conductivity at low frequencies. The second term is composed of two single relaxation terms: $1/(1+j\omega/\omega_P)$ and $1/(1+j\omega/\omega_Q)$.

Hence it is concluded that Eq. 98 for the terlamellar system shows two dielectric relaxations due to the interfacial polarization. The quantities appearing in Eq. 98 are summarized as follows:

$$S = \delta_b + \delta_f + \delta_a = \frac{d_b}{\epsilon_v \varepsilon_b} + \frac{d_f}{\epsilon_v \varepsilon_f} + \frac{d_a}{\epsilon_v \varepsilon_a}$$
$$= \Gamma\left(\frac{1}{C_b} + \frac{1}{C_f} + \frac{1}{C_a}\right), \tag{99}$$

$$R = \frac{\delta_b}{k_b} + \frac{\delta_f}{k_f} + \frac{\delta_a}{k_a} = \frac{d_b}{\kappa_b} + \frac{d_f}{\kappa_f} + \frac{d_a}{\kappa_a} = \Gamma\left(\frac{1}{G_b} + \frac{1}{G_f} + \frac{1}{G_a}\right), \tag{100}$$

$$\Phi = \frac{1}{S}[(k_b - k_a)^2 k_f \delta_b \delta_a + (k_b - k_f)^2 k_a \delta_b \delta_f + (k_a - k_f)^2 k_b \delta_a \delta_f], \tag{101}$$

$$\Phi = \omega_Q \omega_P \eta - k_b \zeta, \tag{102}$$

$$\Lambda = \frac{1}{S}[(k_b - k_a)^2 k_f^2 \delta_b \delta_a + (k_b - k_f)^2 k_a^2 \delta_b \delta_f + (k_a - k_f)^2 k_b^2 \delta_a \delta_f], \tag{103}$$

$$\Lambda = \omega_Q \omega_P (k_b \eta + \zeta) - (\omega_Q + \omega_P) k_b \zeta, \tag{104}$$

$$\eta = -[(k_b - k_a)\delta_a + (k_b - k_f)\delta_f], \tag{105}$$

$$\zeta = -[(k_b - k_a) k_f \delta_a + (k_b - k_f) k_a \delta_f], \tag{106}$$

$$\omega_Q + \omega_P = \frac{1}{S}\left[k_b(\delta_a + \delta_f) + k_f(\delta_b + \delta_a) + k_a(\delta_b + \delta_f)\right] \tag{107}$$
$$= -(A + E),$$

$$\omega_Q\omega_P = \frac{1}{S}(k_b k_a \delta_f + k_b k_f \delta_a + k_a k_f \delta_b) \tag{108}$$

$$= AE - BD,$$

$$\omega_Q = \frac{1}{2}\left[-(A + E) + \sqrt{(A - E)^2 + 4BD}\right], \tag{109}$$

$$\omega_P = \frac{1}{2}\left[-(A + E) - \sqrt{(A - E)^2 + 4BD}\right], \tag{110}$$

The expressions for $A+E$, $A-E$ and BD are already given in Eqs. 24, 25 and 27.

III. PHENOMENOLOGICAL REPRESENTATION AND DEVELOPMENT BY MEANS OF THE LUMPED CIRCUIT MODEL

In this section, the theoretical expressions derived on the basis on electrostatic field laws are connected mathematically with the phenomenological representation based on the C–G circuit models.

3.1 Constitution of Dielectric Relaxations by Means of the Lumped G–C Models[2, 9]

So far, a heterogeneous dielectrics in terlamellar structure has merely been assumed to be a series combination of three phases, each of which is represented routinely by a lumped capacitance-conductance (C–G) model as shown in Fig. 4B.

In this instance, constituent phases b, f and a are related to the respective lumped C–G models by the following relations:

$$C = \epsilon_v \varepsilon \frac{\Gamma}{d} = \frac{\Gamma}{\delta}, \quad G = \kappa\frac{\Gamma}{d} = kC, \quad \frac{\delta}{k} = \frac{\Gamma}{G} = \frac{d}{\kappa}, \tag{111}$$

$$C_b = \epsilon_v \varepsilon_b \frac{\Gamma}{d_b} = \frac{\Gamma}{\delta_b}, \quad C_f = \epsilon_v \varepsilon_f \frac{\Gamma}{d_f} = \frac{\Gamma}{\delta_f},$$

$$C_a = \epsilon_v \varepsilon_a \frac{\Gamma}{d_a} = \frac{\Gamma}{\delta_a}, \tag{112}$$

$$G_b = \kappa_b \frac{\Gamma}{d_b} = k_b C_b, \quad G_f = \kappa_f \frac{\Gamma}{d_f} = k_f C_f,$$

$$G_a = \kappa_a \frac{\Gamma}{d_a} = k_a C_a, \tag{113}$$

$$C^* = C + \frac{G}{j\omega} = C - jC'', \; G^* = j\omega C^* = G + j\omega C = G + jG'', \tag{114}$$

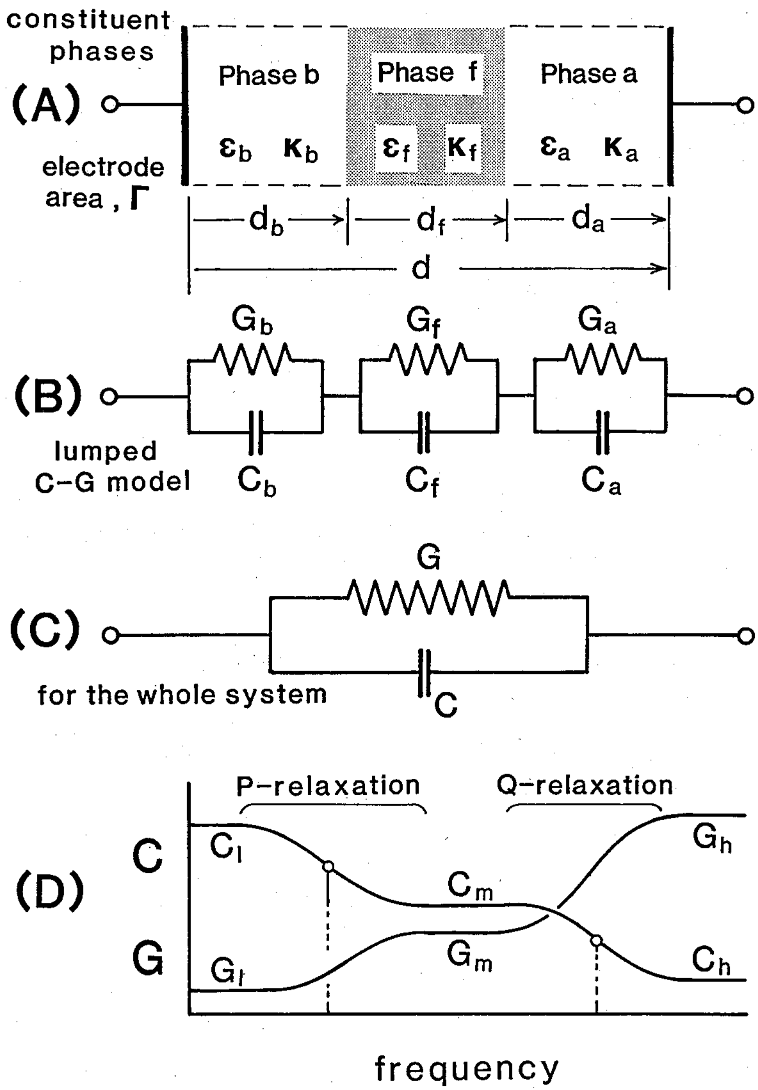


Fig. 4. (A) Dielectrics in terlamellar structure, (B) three corresponding lumped *C-G* circuit models, (C) apparent conductance *G* and capacitance *C* for the whole system, and (D) two dielectric relaxations *P* and *Q* exhibited by the frequency dependence of *C* and *G*.

$$C_b^* = C_b + \frac{G_b}{j\omega}, \quad C_f^* = C_f + \frac{G_f}{j\omega}, \quad C_a^* = C_a + \frac{G_a}{j\omega}, \tag{115}$$

$$G_b^* = G_b + j\omega C_b, \quad G_f^* = G_f + j\omega C_f, \quad G_a^* = G_a + j\omega C_a, \tag{116}$$

$$\varepsilon^* = \varepsilon + \frac{\kappa}{j\omega \epsilon_v}, \quad \kappa^* = j\omega \epsilon_v \varepsilon^* = \kappa + j\omega \epsilon_v \varepsilon, \tag{117}$$

$$\varepsilon_b^* = \varepsilon_b + \frac{\kappa_b}{j\omega\epsilon_v}, \qquad \varepsilon_f^* = \varepsilon_f + \frac{\kappa_f}{j\omega\epsilon_v}, \qquad \varepsilon_a^* = \varepsilon_a + \frac{\kappa_a}{j\omega\epsilon_v}, \tag{118}$$

$$C^* = \epsilon_v\varepsilon^*\frac{\Gamma}{d} = \epsilon_v\left(\varepsilon + \frac{\kappa}{j\omega\epsilon_v}\right)\frac{\Gamma}{d}, \tag{119}$$

$$G^* = \kappa^*\frac{\Gamma}{d} = (\kappa + j\omega\epsilon_v\varepsilon)\frac{\Gamma}{d}, \tag{120}$$

$$C_b^* = \epsilon_v\varepsilon_b^*\frac{\Gamma}{d}, \qquad C_f^* = \epsilon_v\varepsilon_f^*\frac{\Gamma}{d}, \qquad C_a^* = \epsilon_v\varepsilon_a^*\frac{\Gamma}{d}, \tag{121}$$

$$G_b^* = \kappa_b^*\frac{\Gamma}{d_b}, \qquad G_f^* = \kappa_f^*\frac{\Gamma}{d_f}, \qquad G_a^* = \kappa_a^*\frac{\Gamma}{d_a}, \tag{122}$$

For a series combination of three sets of lumped capacitances and conductances as shown in Fig. 4B, the complex capacitance $C^*=C+G/j\omega$ shown by Fig. 4C for the whole system has already been presented as follows[7, 8]:

$$\frac{1}{C^*} = \frac{1}{C_b^*} + \frac{1}{C_f^*} + \frac{1}{C_a^*}, \tag{123}$$

$$C^* = \frac{C_b^*\,C_f^*\,C_a^*}{C_b^*\,C_f^* + C_f^*\,C_a^* + C_a^*\,C_b^*}, \tag{124}$$

$$= \frac{(G_b + j\omega C_b)(G_f + j\omega C_f)(G_a + j\omega C_a)}{\boldsymbol{D}j\omega\left(1 + j\dfrac{\omega}{\omega_Q}\right)\left(1 + j\dfrac{\omega}{\omega_P}\right)}, \tag{125}$$

$$= C_h + \frac{C_l - C_m}{1+j\dfrac{\omega}{\omega_P}} + \frac{C_m - C_h}{1+j\dfrac{\omega}{\omega_Q}} + \frac{1}{j\omega}G_l, \tag{126}$$

$$= C_h + \frac{(C_l - C_m)\,\omega_P}{j\omega + \omega_P} + \frac{(C_m - C_h)\,\omega_Q}{j\omega + \omega_Q} + \frac{1}{j\omega}G_l, \tag{127}$$

$$G^*=j\omega C^*$$

$$= G_l + \frac{(C_l - C_m)\,\omega_P j\dfrac{\omega}{\omega_P}}{1 + j\dfrac{\omega}{\omega_P}} + \frac{(C_m - C_h)\,\omega_Q j\dfrac{\omega}{\omega_Q}}{1 + j\dfrac{\omega}{\omega_Q}} + j\omega C_h, \tag{128}$$

$$C_h = \frac{C_bC_fC_a}{\boldsymbol{A}}, \tag{129}$$

$$C_l = \frac{C_b(G_fG_a)^2 + C_f(G_aG_b)^2 + C_a(G_bG_f)^2}{\boldsymbol{D}^2}, \tag{130}$$

$$C_l - C_m = \frac{\omega_Q\omega_P}{\boldsymbol{D}(\omega_Q - \omega_P)}\left(-E + \frac{1}{\omega_P}F + \omega_p C_bC_fC_a - \frac{1}{\omega_P^2}G_bG_fG_a\right), \tag{131}$$

$$C_m - C_h = \frac{\omega_Q\omega_P}{\boldsymbol{D}(\omega_Q - \omega_P)}\left(E - \frac{1}{\omega_Q}F - \omega_Q C_bC_fC_a + \frac{1}{\omega_Q^2}G_bG_fG_a\right), \tag{132}$$

$$C_l - C_h = \frac{1}{AD^2}\left[C_bG_b^2 (C_fG_a - C_aG_f)^2 + C_fG_f^2 (C_aG_b - C_bG_a)^2 + C_aG_a^2 (C_bG_f - C_fG_b)^2 \right], \tag{133}$$

$$G_l = \frac{G_bG_fG_a}{D}, \tag{134}$$

$$G_h = \frac{G_b (C_fC_a)^2 + G_f (C_aC_b)^2 + G_a (C_bC_f)^2}{A^2}, \tag{135}$$

$$\omega_P = \frac{B - \sqrt{B^2 - 4AD}}{2A} = \frac{2D}{B + \sqrt{B^2 - 4AD}}, \tag{136}$$

$$\omega_Q = \frac{B + \sqrt{B^2 - 4AD}}{2A} = \frac{2D}{B - \sqrt{B^2 - 4AD}}, \tag{137}$$

$$\omega_Q + \omega_P = \frac{B}{A},\ \omega_Q\omega_P = \frac{D}{A}, \tag{138}$$

$$A = C_bC_f + C_fC_a + C_aC_b, \tag{139}$$

$$B = C_b (G_f + G_a) + C_f (G_a + G_b) + C_a (G_b + G_f), \tag{140}$$

$$D = G_bG_f + G_fG_a + G_aG_b, \tag{141}$$

$$E = C_bC_fG_a + C_fC_aG_b + C_aC_bG_f, \tag{142}$$

$$F = C_bG_fG_a + C_fG_aG_b + C_aG_bG_f, \tag{143}$$

$$\begin{aligned} B^2 - 4AD = & (C_bG_f - C_fG_b)^2 + (C_fG_a - C_aG_f)^2 + (C_aG_b - C_bG_a)^2 \\ & - 2 (C_bG_f - C_fG_b) (C_fG_a - C_aG_f) - 2 (C_fG_a - C_aG_f) (C_aG_b - C_bG_a) \\ & - 2 (C_aG_b - C_bG_a) (C_bG_f - C_fG_b). \end{aligned} \tag{144}$$

In connection with the symbols used in the preceding section II 2.3, we have the following formulas:

$$S \equiv \delta_b + \delta_f + \delta_a = \Gamma\left(\frac{1}{C_b} + \frac{1}{C_f} + \frac{1}{C_a} \right), \tag{145}$$

$$\frac{\Gamma}{S} = \frac{C_bC_fC_a}{C_bC_f + C_fC_a + C_aC_b} = \frac{C_bC_fC_a}{A} = C_h, \tag{146}$$

$$R \equiv \frac{d_b}{\kappa_b} + \frac{d_f}{\kappa_f} + \frac{d_a}{\kappa_a} = \Gamma\left(\frac{1}{G_b} + \frac{1}{G_f} + \frac{1}{G_a} \right), \tag{147}$$

$$\frac{\Gamma}{S} = \frac{G_bG_fG_a}{G_bG_f + G_fG_a + G_aG_b} = \frac{G_bG_fG_a}{D} = G_l, \tag{148}$$

$$\begin{aligned} & (j\omega C_b + G_b)(j\omega C_f + G_f) + (j\omega C_f + G_f)(j\omega C_a + G_a) \\ & \quad + (j\omega C_a + G_a)(j\omega C_b + G_b) \\ & = A (j\omega)^2 + Bj\omega + D = A\left[(j\omega)^2 + \frac{B}{A}j\omega + \frac{D}{A}\right], \end{aligned} \tag{149}$$

$$= A\,[(j\omega)^2 + (\omega_Q + \omega_P)j\omega + \omega_Q\omega_P] = A\,(j\omega + \omega_Q)(j\omega + \omega_P). \tag{150}$$

It is readily seen from Eqs. 126 and 128 that the whole circuit system consisting of three lumped C–G models shown in Fig. 4B has two dielectric relaxations, the frequency profile of C and G being shown schematically in Fig. 4D.

3.2 Equivalence between the Field Theory and the Circuit Model—Proof I

In the first instance (Proof I), a proof will be shown that ε^* derived in the field theory leads to C^* defined in the circuit model.

By use of Eqs. 83 and 85 in turn, Eq. 119 is rearranged as

$$C^* = \varepsilon^* \frac{\epsilon_v \Gamma}{d} = \Gamma \frac{j\omega + k_b}{j\omega V} Q_b. \tag{151}$$

Substituting Eq. 76 for Q_b, Eq. 67 for σ_a, and Eq. 146 for Γ/S in Eq. 151, and rearranging the subsequent formulas with perseverance, we have the following.

$$C^* = \Gamma \frac{j\omega + k_b}{j\omega V} \cdot \frac{1}{S}[-(\delta_a + \delta_f)\sigma_b - \delta_a\sigma_a + V] \tag{152}$$

$$= \frac{\Gamma}{S} \cdot \frac{j\omega + k_b}{j\omega V}\left[-\frac{(\delta_a + \delta_f)(k_b - k_f)(j\omega + k_a)}{S(j\omega + \omega_Q)(j\omega + \omega_P)}V + \frac{\delta_a(k_a - k_f)(j\omega + k_b)}{S(j\omega + \omega_Q)(j\omega + \omega_P)}V + V\right] \tag{153}$$

$$= \frac{\Gamma(j\omega + k_b)(j\omega + k_f)(j\omega + k_a)}{j\omega S(j\omega + \omega_Q)(j\omega + \omega_P)}$$

$$= \frac{C_b C_f C_a (j\omega + k_b)(j\omega + k_f)(j\omega + k_a)}{A j\omega (j\omega + \omega_Q)(j\omega + \omega_P)}$$

$$= \frac{(j\omega C_b + G_b)(j\omega C_f + G_f)(j\omega C_a + G_a)}{j\omega A(j\omega + \omega_Q)(j\omega + \omega_P)}. \tag{154}$$

By use of Eq. 150, Eq. 154 is rearranged to

$$C^* = \frac{C_b^* C_f^* C_a^*}{C_b^* C_f^* + C_f^* C_a^* + C_a^* C_b^*}. \tag{155}$$

This final Eq. 155 is the same as Eq. 124 which is derived for the circuit model shown in Fig. 4B.

3.3 Equivalence between the Field Theory and the Circuit Model—Proof II

In the second instance (Proof II), a different proof will be shown by way of a double relaxation term $1/[(j\omega+\omega_Q)(j\omega+\omega_P)]$.

3.3.1. Rearrangement from the circuit model

Equation 126 containing two single relaxation terms is rearranged to the following expressions with a double relaxation term by assuming two undetermined parameters ϕ and λ, which are to be determined in Eqs. 163 and 164 later on:

$$C^* = C_h + \frac{(C_l - C_m)\,\omega_P}{j\omega + \omega_P} + \frac{(C_m - C_h)\,\omega_Q}{j\omega + \omega_Q} + \frac{1}{j\omega}G_l \tag{156}$$

$$= C_h + \frac{j\omega\phi + \lambda}{(j\omega + \omega_Q)(j\omega + \omega_P)} + \frac{1}{j\omega}G_l \tag{157}$$

$$= \frac{C_h j\omega(j\omega + \omega_Q)(j\omega + \omega_P) + j\omega(j\omega\phi + \lambda) + G_l(j\omega + \omega_Q)(j\omega + \omega_P)}{j\omega(j\omega + \omega_Q)(j\omega + \omega_P)}$$

$$= \frac{(j\omega)^3 C_h + (j\omega)^2\left(G_l + \phi + C_h\frac{\boldsymbol{B}}{\boldsymbol{A}}\right) + j\omega\left(G_l\frac{\boldsymbol{B}}{\boldsymbol{A}} + \lambda + C_h\frac{\boldsymbol{D}}{\boldsymbol{A}}\right) + G_l\frac{\boldsymbol{D}}{\boldsymbol{A}}}{j\omega(j\omega + \omega_Q)(j\omega + \omega_P)}. \tag{158}$$

In order to determine the two parameters ϕ and λ, the original Eq. 124 for the circuit model is rearranged, by use of Eq. 150, as follows:

$$C^* = \frac{1}{j\omega}\cdot\frac{(j\omega C_b + G_b)(j\omega C_f + G_f)(j\omega C_a + G_a)}{(j\omega C_b + G_b)(j\omega C_f + G_f) + (j\omega C_f + G_f)(j\omega C_a + G_a) + (j\omega C_a + G_a)(j\omega C_b + G_b)}$$

$$= \frac{(j\omega C_b + G_b)(j\omega C_f + G_f)(j\omega C_a + G_a)}{j\omega \boldsymbol{A}(j\omega + \omega_Q)(j\omega + \omega_p)} \tag{159}$$

$$= \frac{\frac{C_bC_fC_a}{\boldsymbol{A}}(j\omega)^3 + \frac{\boldsymbol{E}}{\boldsymbol{A}}(j\omega)^2 + \frac{\boldsymbol{F}}{\boldsymbol{A}}j\omega + \frac{G_bG_fG_a}{\boldsymbol{A}}}{j\omega(j\omega + \omega_Q)(j\omega + \omega_P)}. \tag{160}$$

Comparison between Eqs. 160 and 158 leads to the following:

$$C_h = \frac{C_bC_fC_a}{\boldsymbol{A}}, \tag{161}$$

$$G_l = \frac{G_bG_fG_a}{\boldsymbol{D}}, \tag{162}$$

$$\phi = \frac{\boldsymbol{E}}{\boldsymbol{A}} - C_h\frac{\boldsymbol{B}}{\boldsymbol{A}} - G_l, \tag{163}$$

$$\lambda = \frac{\boldsymbol{F}}{\boldsymbol{A}} - C_h\frac{\boldsymbol{D}}{\boldsymbol{A}} - G_l\frac{\boldsymbol{B}}{\boldsymbol{A}}. \tag{164}$$

3.3.2 *Rearrangement from the field theory*

By using Eqs. 97, 146, 148 in turn, Eq. 119 is rearranged to the following:

$$C^* = \frac{\Gamma}{S} + \frac{\Gamma}{S^2\omega_Q\omega_P}\cdot\frac{j\omega\Phi + \Lambda}{(j\omega + \omega_Q)(j\omega + \omega_P)} + \frac{\Gamma}{j\omega R}, \tag{165}$$

$$= C_h + \frac{\Gamma}{S^2\omega_Q\omega_P}\cdot\frac{j\omega\Phi + \Lambda}{(j\omega + \omega_Q)(j\omega + \omega_P)} + \frac{1}{j\omega}G_l. \tag{166}$$

The former part of the second term in Eq. 166 is rearranged by use of Eqs. 101, 57, 13, 14 and 139–143 in turn as follows:

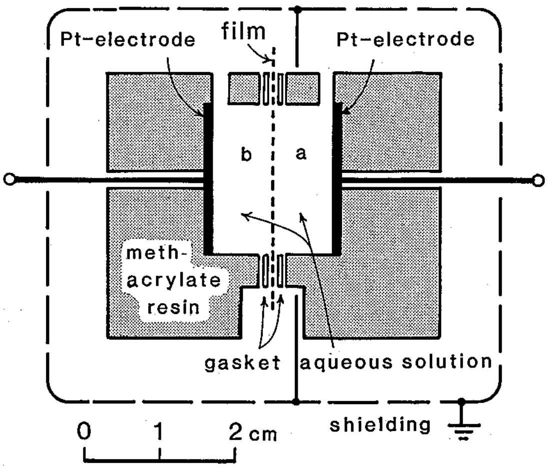


Fig. 5. Cell system for measuring the impedance of a solution-film-solution system.

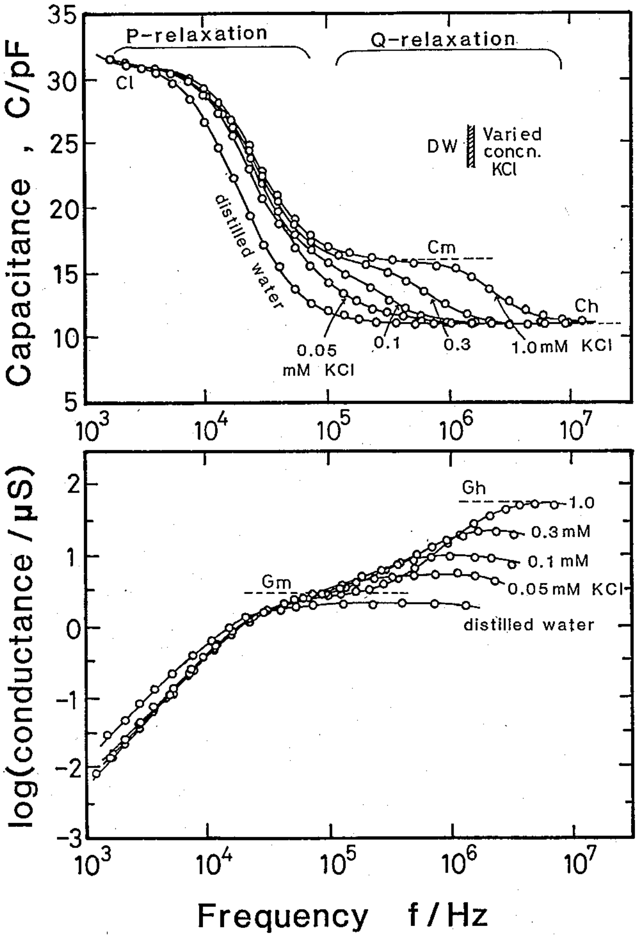


Fig. 6. Frequency dependence of the capacitance C and the conductance G for the whole systems composed of the aqueous Phase b (DW) and the aqueous Phase a (DW, 0.05, 0.1, 0.3 or 1 mM KCl solution).

$$\frac{\Gamma\Phi}{S^2\omega_Q\omega_P}$$

$$= \frac{\Gamma}{S^2} \cdot \frac{(k_b - k_a)^2 k_f \delta_b \delta_a + (k_b - k_f)^2 k_a \delta_b \delta_f + (k_a - k_f)^2 k_b \delta_a \delta_f}{k_b k_a \delta_f + k_b k_f \delta_a + k_a k_f \delta_b} \tag{167}$$

$$= \frac{\Gamma^2}{S^2} \cdot \frac{\left(\frac{G_b}{C_b} - \frac{G_a}{C_a}\right)^2 G_f + \left(\frac{G_b}{C_b} - \frac{G_f}{C_f}\right)^2 G_a + \left(\frac{G_a}{C_a} - \frac{G_f}{C_f}\right)^2 G_b}{G_b G_a + G_a G_f + G_f G_b}. \tag{168}$$

After tiresome rearrangement, Eq. 168 is simplified to the following:

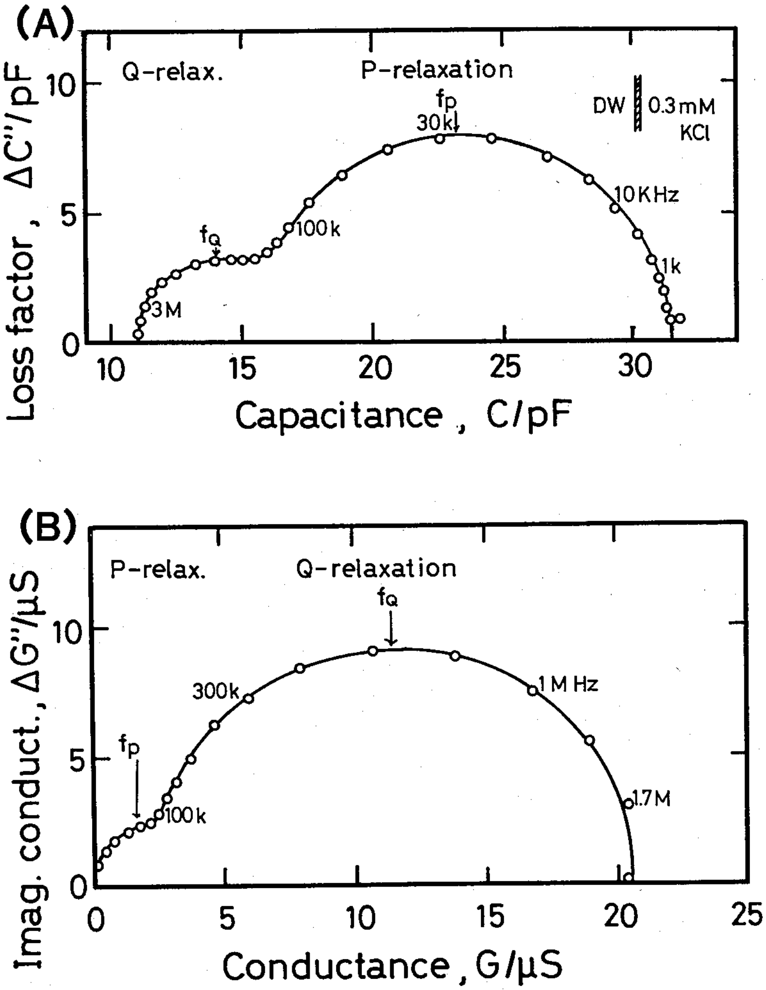


Fig. 7. Complex plane plots of (A) the complex capacitance C^* [C, $\Delta C''=(G-G_l)/(2\pi f)$] and (B) the complex conductance G^* [G, $\Delta G''=2\pi f(C-C_h)$] for the whole system composed of DW-Teflon film-0.3 mM KCl. The data referring to the part of Fig. 6.

$$\frac{\Gamma\Phi}{S^2\omega_Q\omega_P} = \frac{\boldsymbol{EAD} - C_bC_fC_h\boldsymbol{BD} - G_bG_fG_a\boldsymbol{A}^2}{\boldsymbol{A}^2\boldsymbol{D}} \tag{169}$$

$$= \frac{\boldsymbol{E}}{\boldsymbol{A}} - C_h\frac{\boldsymbol{B}}{\boldsymbol{A}} - G_l = \phi. \tag{170}$$

In a similar manner, the latter part of the second term in Eq. 166 is rearranged as follows:

$$\frac{\Gamma\Lambda}{S^2\omega_Q\omega_P}$$

$$= \frac{\Gamma}{S^2}\cdot\frac{(k_b-k_a)^2k_f^2\delta_b\delta_a + (k_b-k_f)^2k_a^2\delta_b\delta_f + (k_a-k_f)^2k_b^2\delta_a\delta_f}{k_bk_a\delta_f + k_bk_f\delta_a + k_ak_f\delta_b} \tag{171}$$

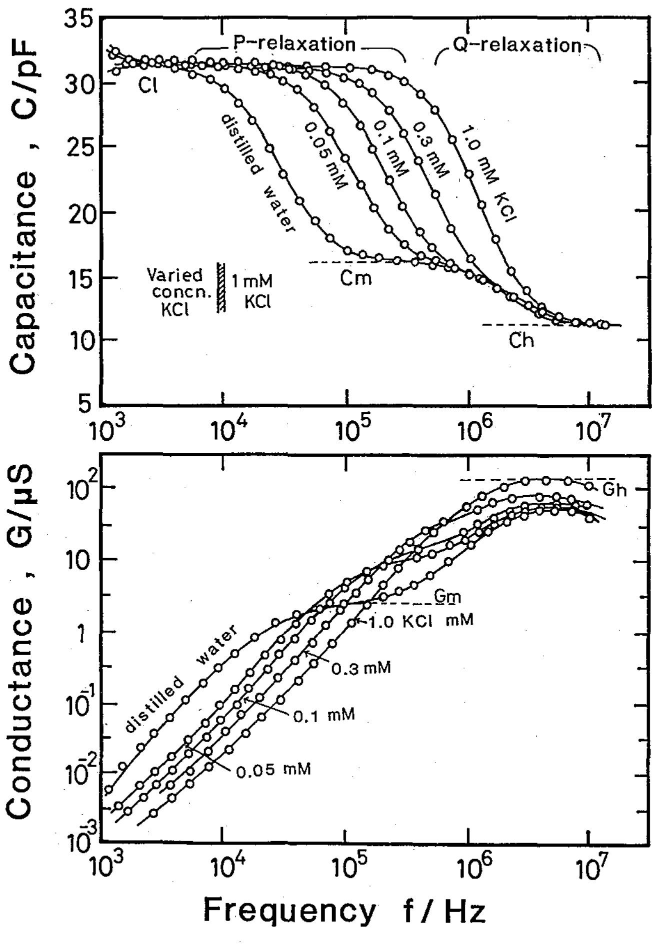


Fig. 8. Frequency dependence of the capacitance C and the conductance G for the whole systems composed of Phase b (DW, 0.05, 0.1, 0.3 or 1 mM KCl) and Phase a (1 mM KCl).

$$= \frac{\Gamma^2}{S^2 \boldsymbol{D}} \left[\left(\frac{G_b}{C_b} - \frac{G_a}{C_a} \right)^2 \frac{G_f^2}{C_f} + \left(\frac{G_b}{C_b} - \frac{G_f}{C_f} \right)^2 \frac{G_a^2}{C_a} + \left(\frac{G_a}{C_a} - \frac{G_f}{C_f} \right)^2 \frac{G_b^2}{C_b} \right], \tag{172}$$

$$= \frac{\boldsymbol{FAD} - C_b C_f C_a \boldsymbol{D}^2 - G_b G_f G_a \boldsymbol{BA}}{\boldsymbol{A}^2 \boldsymbol{D}}, \tag{173}$$

$$= \frac{\boldsymbol{F}}{\boldsymbol{A}} - C_h \frac{\boldsymbol{D}}{\boldsymbol{A}} - G_l \frac{\boldsymbol{B}}{\boldsymbol{A}} = \lambda. \tag{174}$$

To sum up Eqs. 174, 170, 166 and 155, the expression of ε^* derived on the basis of the field theory leads to C^* formulated for the lumped C–G model. It is thus concluded for

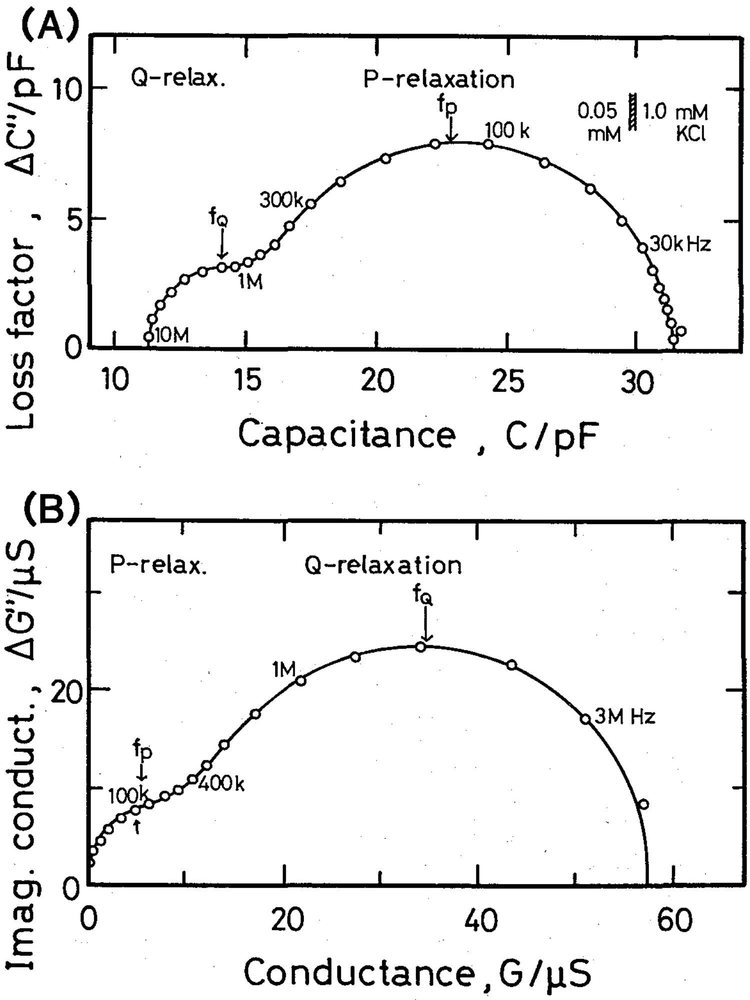


Fig. 9. Complex plane plots of (A) the complex capacitance C^* $[C, \Delta C''=(G-G_l)/(2\pi f)]$ and (B) the complex conductance G^* $[G, \Delta G''=2\pi f(C-C_h)]$ for the whole system composed of 0.05 mM-Teflon film-1 mM KCl. The data referring to the part of Fig. 8.

the terlamellar structure that one can choose either ε^*-representation or C^*-representation at one's convenience.

IV. OBSERVATION OF DIELECTRIC RELAXATIONS FOR TERLAMELLAR SYSTEMS AND SOME ANALYSIS BASED ON THE LUMPED C-G MODELS

4.1 Measurement for Triphase Systems

By use of an LF Impedance Analyser Model 4192A made by Hewlett-Packard Co., Ltd., dielectric measurements were carried out at 25°C for the systems in which a Teflon film is sandwiched between two aqueous phases b and a as depicted in Fig. 5.

Table 1. Dielectric Parameters Observed and Phase Parameters Calculated for KCl(b)-Teflon(f)-KCl(a) Systems at 25°C

Specimen name	Constituent Phase b, Phase a KCl/mM		Dielectric parameters observed						
			C_l / pF	C_m / pF	C_h / pF	G_m / μS	G_h / μS	f_p / kHz	f_Q / kHz
DTD	DW	DW	31.2	···	10.9	···	2.60	19.8	···
DTK0.05	DW	0.05	31.3	15.1	10.9	2.72	5.81	29.8	123.
DTK0.1	DW	0.1	31.5	15.5	11.0	2.76	9.69	28.9	235.
DTK0.3	DW	0.3	31.4	16.2	11.0	2.72	20.9	29.8	537.
DTK1	DW	1.0	31.4	16.2	11.2	2.60	58.6	27.7	1460.
K0.05TK1	0.05	1.0	31.3	16.0	11.3	11.2	58.8	120.0	1911.
K0.1TK1	0.1	1.0	31.3	16.1	11.2	20.4	68.6	224.0	1542.
K0.3TK1	0.3	1.0	31.3	15.9	11.2	51.1	84.6	539.0	1214.
K1TK1	1.0	1.0	31.2	···	11.1	···	141.0	···	1257.

	Composite Phase ba				Phase parameters calculated							
	$C_{ba,l}$ / pF	$C_{ba,h}$ / pF	$G_{ba,l}$ / μS	$G_{ba,h}$ / μS	C_f / pF	G_f / μS	C_b / pF	G_b / μS	C_a / pF	G_a / μS	f_p / kHz	f_Q / kHz
DTD	···	16.8	···	6.14	31.22	0.00	33.6	12.2	33.6	12.2	20.4	···
DTK0.05	23.9	16.9	8.32	13.6	31.22	0.00	35.7	10.5	32.1	40.5	23.3	141.
DTK0.1	26.9	16.9	9.68	22.6	31.22	0.00	34.6	11.1	33.0	76.3	25.9	255.
DTK0.3	31.0	16.9	10.6	50.5	31.22	0.00	34.7	11.2	33.1	182	26.6	595.
DTK1	33.0	17.5	11.0	140	31.22	0.00	35.7	11.2	34.3	572	26.6	1783.
K0.05TK1	30.3	17.6	44.2	148	31.22	0.00	35.8	48.2	34.6	529	112	1676.
K0.1TK1	27.6	17.6	75.4	173	31.22	0.00	35.4	86.2	34.9	598	199	1912.
K0.3TK1	21.7	17.6	169	212	31.22	0.00	41.5	254	30.7	502	492	1870.
K1TK1	···	17.3	···	349	31.22	0.00	34.6	699	34.6	699	···	1121.

Teflon film thickness, d_f=0.193 mm; film area, Γ=3.142 cm^2; compartment depth, d_b=6.60 mm, d_a=6.73 mm. Values of G_l were too small to be observed with accuracy.

By use of Eq. 112, capacitance values lead to the associated permittivities as follows:

C_f=31.22 ; ε_b=2.167

C_b=33.6−35.8 ; ε_b=79.8~85.0

C_a=32.1−34.9 ; ε_a=77.7~84.5

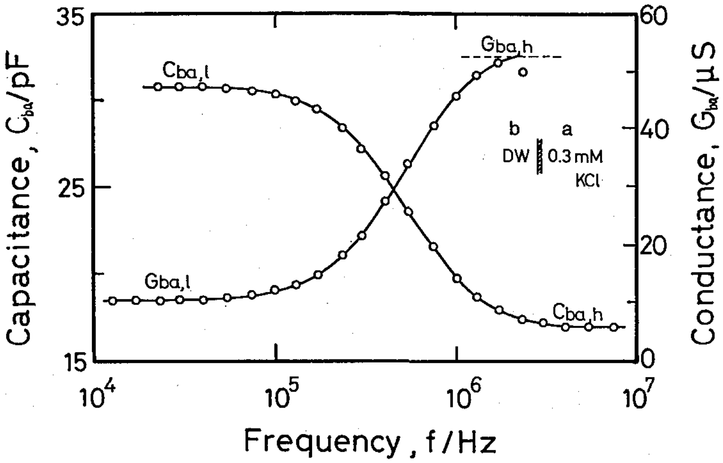


Fig. 10. Frequency dependence of the capacitance C_{ba} and the conductance G_{ba} for the composite Phase *ba* composed of Phase *b* (DW) and Phase *a* (0.3 mM KCl). Values of C_{ba} and G_{ba} were calculated from observed values of C_f^* and C^* at each frequency by use of the expression $C_{ba}^* = C_f^* C^* / (C_f^* - C^*)$.

The first series of observations is that the left side aqueous (aq) phase *b* is kept distilled water (D.W.) and the right side aq phase *a* is changed from D.W. to 0.05, 0.1, 0.3 and 1 mM KCl solutions in turn. The observed results are shown in Fig. 6, the complex capacitance and conductance plane plots being shown in Fig. 7. Two dielectric relaxations *P* and *Q* are found in common. A system with D.W.-D.W. aq phases (abbreviated to DTD) keeps a single relaxation profile. When the right side aq phase of the cell is changed to 0.05, 0.1, 0.3, and 1 mM KCl solutions in turn, *Q*-relaxation shifts to higher frequencies, *P*-relaxation remaining unchanged.

The second series of observations is that the right side aq phase *a* is kept a 1 mM KCl solution and the left side aq phase *b* is changed from 1 mM to 0.3, 0.1, 0.05 mM KCl and D.W. in turn. The observed results are shwon in Fig. 8, the complex capacitance and conductance plane plots being shown in Fig. 9. In this series, a system with 1 mM-1 mM aq phases (K1TK1) keeps a single relaxation profile. With the decrease in the KCl concentration in the left side aq phase *b* of the cell, *P*-relaxaton shifts to lower frequencies, *Q*-relaxation remaining unchanged.

The values of C_l, C_m, C_h, G_l, G_m, G_h, f_P and f_Q are obtained from Figs. 6–9 of the observations, being listed in Table 1.

4.2 Numerical Analysis based on the lumped C–G Model

The Teflon film intervening between Phases *b* and *a* is perfectly insulating, the capacitance C_f being very stable and $G_f=0$ irrespective of ambient aq phases. Hence the following simplified analysis is admissible.

Following the viewpoint of the lumped C–G circuit models, the D.W.-Teflon film-D.W. system (DTD) with the cell shown in Fig. 5 is understood to be a series combination of two phases: one is a Teflon film phase *f*, another being a composite aq Phase (termed *ba*) of two Phases *b* and *a*. Hence a single relaxation is reasonably observed as seen in Fig. 6. Capacitance C_{ba} and conductance G_{ba} for this Phase *ba* is readily evaluated by use of the formulas and the procedure explained in Appendix I. Thus, we obtain $C_f=31.22$ pF, $G_f=0$ μS, $C_{ba}=16.81$ pF$=C_b/2 \doteqdot C_a/2$, and $G_{ba}=6.143$ μS, provided the two compartments *b* and *a* are of the same size as each other. It is assumed hereafter that the values obtained for C_f and G_f of Teflon Phase *f* hold also for other systems.

Two dielectric relaxations *P* and *Q* are observed in the systems where Phases *b* and *a* are different from each other in KCl concentration. Complex capacitance C_{ba}^* of the composite Phase *ba* of two Phase *b* and *a* can be expressed as

$$\frac{1}{C_b^*}+\frac{1}{C_a^*}=\frac{1}{C_{ba}^*}=\frac{1}{C^*}-\frac{1}{C_f^*}. \tag{175}$$

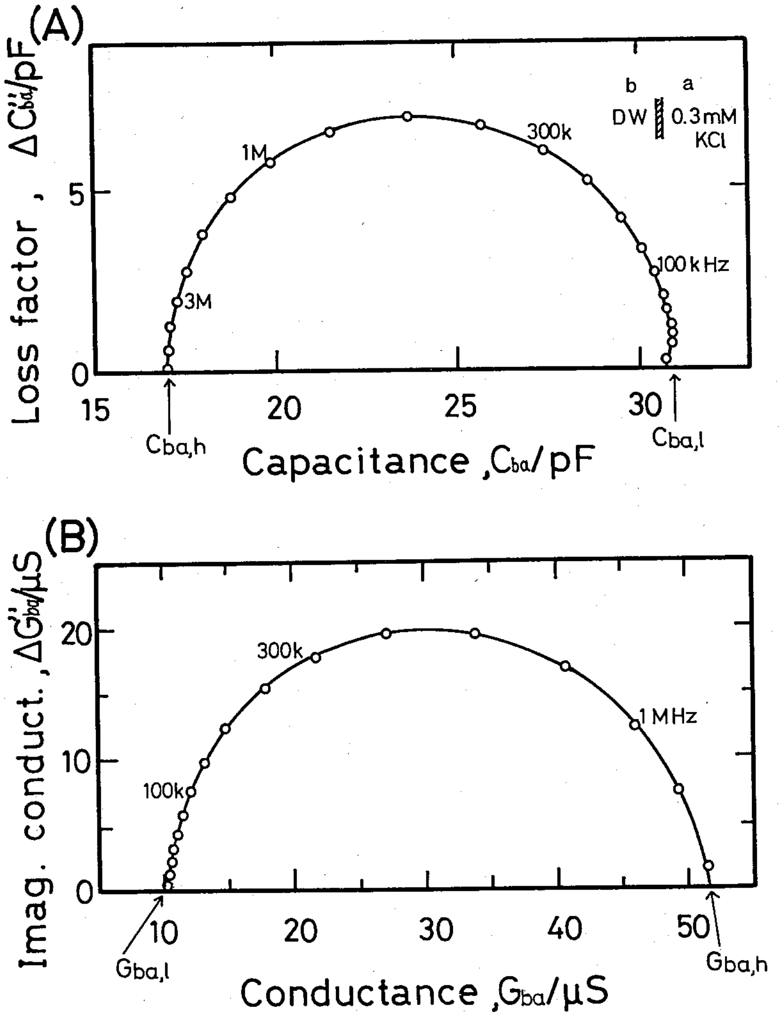


Fig. 11. Complex plane plots of (A) the complex capacitance C_{ba}^* [C_{ba}, $\Delta C_{ba}''=(G_{ba}-G_{ba,l})/(2\pi f)$] and (B) the complex conductance G_{ba}^* [G_{ba}, $\Delta G_{ba}''=2\pi f(C_{ba}-C_{ba,h})$] for the composite Phase *ba* composed of Phase *b* (DW) and Phase *a* (0.3 mM KCl). The data referring to Fig. 10.

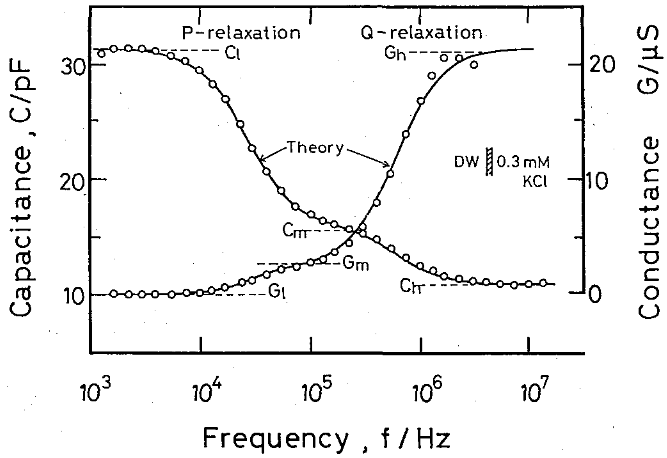


Fig. 12. Comparison between the theoretical curves and the observed values of capacitance C and conductance G for the whole system consisting of DW-Teflon film-0.3 mM KCl. The curves are calculated from the phase parameters C_f, G_f, C_b, G_b, C_a and G_a tabulated in Table 1 by use of Eq. 126.

Using Eq. 174, values of $C_{ba}^* = C_{ba}(\omega) + G_{ba}(\omega)/(j\omega)$ are calculated from observed values of $C^* = C(\omega) + G(\omega)/(j\omega)$ and $C_f = 31.22$ pF and $G_f = 0$ μS at each frequency. The results of C_{ba}^* obtained for the D.W.-Teflon-KCl (0.3 mM) (abbreviated to DTK0.3) system are shown in Figs. 10 and 11, in which one finds a single relaxation ascribable to series combination of C_b^* (Phase b) and C_a^* (Phase a).

Inspection of these C_{ba}^*-profile yields values of $C_{ba,\,l}$, $C_{ba,\,h}$, $G_{ba,\,l}$, $G_{ba,\,h}$ and $f_{ba,\,0}$, where the subscripts l and h mean the limiting values at low and high frequencies respectively. By means of the procedure explained in Appendix I, values of C_b, C_a, G_b, G_a and $f_{ba,\,0}$ are readily calculated from $C_{ba,\,l}$, $C_{ba,\,h}$, $\mathrm{G}_{\mathrm{ba,1}}$ and $G_{ba,\,h}$, the values being listed in Table 1.

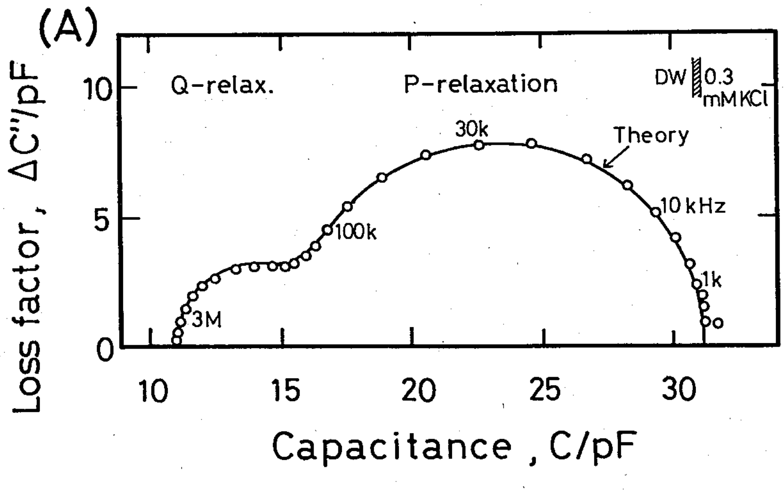
In the last instance, frequency dependence of C and G for the whole system can be calculated from C_b, C_a, C_f, G_b, G_a and G_f listed in Table 1 by use of Eq. 124 or Eq. 126. Examples of the calculation are shown in Figs. 12 and 13, where satisfactory agreements are seen among the calculated curves by Eq. 126 and the values observed. Hence it is concluded that the profiles of frequency dependence of dielectric materials processing conductive properties are well simulated by the lumped C–G circuit model of Fig. 4B.

The values of ε_f, ε_b and ε_a calculated from C_f, C_b and C_a are in conformity with those of Teflon and water as shown in Table 1.

4.3 General Conclusion and Future Problems

It has now been shown in the present study that the dielectric relaxation pattern of Eq. 97 based on the electrostatic field laws is equivalent to that of Eq. 124 developed by means of the lumped C–G circuit models.

As a matter of data analysis, the lumped C–G circuit model is more comprehensible and more effective to treat the observed data than the electrostatic field constitution. Underwater membranes of simple nature like Teflon films are conveniently analysed by



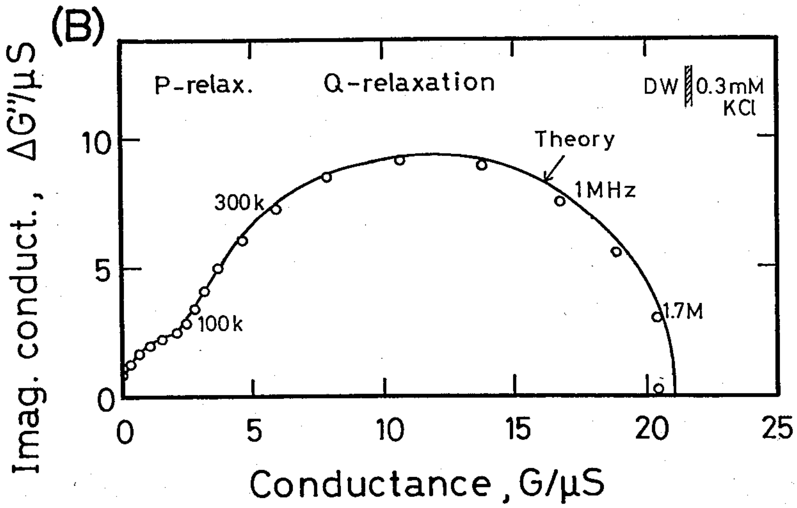


Fig. 13. Comparison between the theoretical curves and the observed values on the complex planes of (A) C—$\Delta C''$ and (B) G—$\Delta G''$ for the whole system of DW-Teflon film-0.3 mM KCl. The curves are calculated by use of Eq. 126. The data referring to Fig. 10.

means of the equivalent C-G circuit model.

On the other hand, membranes of industrial importance such as ion-exchange membranes and reverse osmotic membranes have been investigated extensively from electrochemical and dielectric points of view. Ion selectivity and substance separability of these functional membraes are discussed by measn of the microscopic structure and processes governed by electrostatic and thermodynamic laws. No equivalent circuit models have been shown for these membrane phenomena yet. The circuit-modeling of these functional membranes remains a problem for future exploration

APPENDIX

I. CALCULATION OF PHASE PARAMETERS FROM THE DIELECTRIC PARAMETERS FOR BILAMELLAR STRUCTURE[10, 11]

A diphase system consisting of Phases b and a in bilamellar structure is depicted in Fig. A1 with a series combination of the lumped C_b-G_b and C_a-G_a circuit model. The diphase system shows a single dielectric relaxation profile as shown in Fig. A1. According to a previous investigation, the phase parameters such as C_b, C_a, G_b and G_a are readily calculated from the observed dielectric parameters such as C_l, C_h, G_l and G_h by means of the following expressions:

$$A = \left[\left(1 - \frac{G_l}{G_h}\right)^{-1} - \left(\frac{C_l}{C_h} - 1\right)^{-1}\right]\left(\frac{C_l}{C_h} - 1\right)^{1/2}, \tag{A1}$$

$$Y_a = \frac{1}{2} - \frac{1}{2}\left[1 + \left(\frac{2}{A}\right)^2\right]^{-1/2}, \tag{A2}$$

$$C_a = \frac{C_h}{Y_a}, \tag{A3}$$

$$C_b = \frac{C_h}{1 - Y_a}, \tag{A4}$$

$$X_a = Y_a + \left[Y_a(1 - Y_a)\left(\frac{C_l}{C_h} - 1\right)\right]^{1/2} \quad \text{for} \quad A > 0, \tag{A5}$$

$$X_a = Y_a - \left[Y_a(1 - Y_a)\left(\frac{C_l}{C_h} - 1\right)\right]^{1/2} \quad \text{for} \quad A < 0, \tag{A6}$$

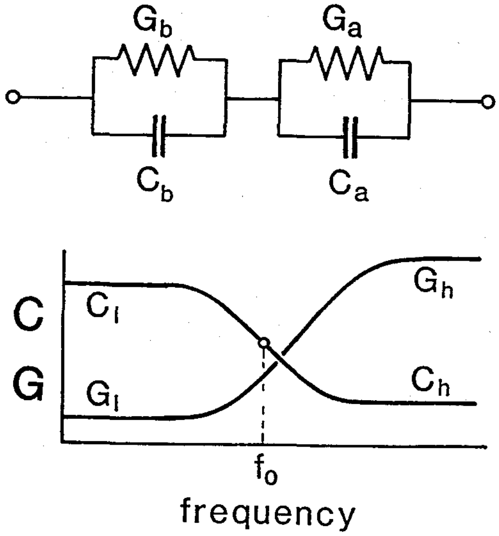


Fig. A1. A series combination of parallel C-G circuit models (upper part) and the frequency dependence for the whole system (lower part).

$$G_a = \frac{G_l}{X_a}, \tag{A7}$$

$$G_b = \frac{G_l}{1 - X_a}, \tag{A8}$$

$$\omega_0 = 2\pi f_0 = \frac{G_h - G_l}{C_l - C_h}. \tag{A9}$$

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