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Dielectric Relaxation of Heterogeneous Systems with Planar Structure—Influence of the Number and the Electric Conductivity of Constituent Phases on the Relaxation Pattern

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平面结构非均匀体系的介电驰豫
——组成相的数目与电导对弛豫的影响[①]

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摘要　非均匀体系在0.1 kHz～10 MHz 频率范围显示出显著的介电弛豫,为了弄清介电弛豫的原因以及该弛豫与非均匀体系界面数目的关系,本文从介电的观点在理论及实验两方面讨论了典型的非均匀体系的例子:膜/溶液体系.特别地,对频率域的介电弛豫谱与组成相的结构及浓度的关系进行了分析,并在Maxwell-Wagner 机理的基础上现象论地解释了弛豫的原因.非均匀体系的介电弛豫性质具有下列特征:(1)介电弛豫数目等于体系内界面种类的数目;(2)特征弛豫频率紧密地依存于溶液相的电导.

关键词　界面极化,介电弛豫,非均匀体系,三层结构

Dielectric Relaxation of Heterogeneous Systems with Planar

Structure——Influence of the Number and the Electric Conductivity

of Constituent Phases on the Relaxation Pattern[①]

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Abstract   Heterogeneous systems exhibit a marked dielectric relaxation at frequencies between 0. 1 kHz and 10 MHz. In order to understand the reason for dielectric relaxation and the relation between the dielectric relaxation and the number of interfaces in heterogeneous systems, as an example of typical heterogeneous systems, film-solution systems are discussed both theoretically and experimentally from dielectric point of view. In particular, the frequency profiles of the dielectric relaxation are analyzed in connection with the structure of the systems and concentration of the constituent phases. The reason for the relaxation is represented through phenomenologically based on the M-W mechanism. The feature of dielectric relaxation of these systems leads to the following characteristics: (1)The number of dielectric relaxations is equal to that of the kind of interfaces; (2) The characteristic frequency of dielectric relaxation are strongly related to the electrical conductivity of the solution phases.

Key words   Interfacial polarization, Dielectric relaxation, Heterogeneous systems, Terlamellar structure

INTRODUCTION

The dielectric spectroscopy method occupies a special place among numerous modern methods used for physical and chemical analyses of material properties, because it can provide important and sometimes unique information on the electrical and structural properties of the systems being studied. In particular, the dielectric study on heterogeneous systems is of practical as well as fundamental importance since information on the internal structure and properties of constituent phases can be

obtained without disturbing the systems. It is known in principle that heterogeneous systems show dielectric relaxation due to interfacial polarization under an alternating electric field. Such a dielectric relaxation was first pointed out by Maxwell[1] and afterwards formulated by Wagner[2] in a convenient form in comparison with experiments. According to the M-W mechanism, in heterogeneous systems composed of some phases, mobile electric charges accumulate on the boundary surfaces between the constituent phases under an applied electric field. This charge accumulation is called interfacial polarization and gives rise to dielectric relaxation. The dielectric relaxation of heterogeneous systems is a delayed response of interfacial polarization to changing stimulus which is almost always an electric field. The relaxation is characterized by a relaxation frequency connected with the time lag between the electric field and polarization, and is often shown as a frequency dependent on electrical properties of the systems being defined by two important parameters: dielectric constant ε(or capacitance C) and electric conductivity κ(or conductance G). A number of examples are readily found in the follow systems: emulsions, suspensions, lipid vesicles, polymer membrane-aqueous solution systems, and the like[3~8]. Although these results have been successfully expressed by the use of theoretical analysis based on the M-W mechanism of interfacial polarization. It is necessary to study and discuss numerous chemical systems to realize the cause of the dielectric relaxation and elucidate the relationship between dielectric relaxation and the number of interfaces of the heterogeneous systems with planar structure.

In the present paper, some simulations based on the lumped C-G models for the planar terlamellar systems were performed. The relationship between the characteristics of dielectric relaxation and the structure of constituent phases is discussed in detail. Furthermore, as the simplest example of heterogeneous systems with planar structure, a practical triphase system of a Teflon film sandwiched between two aqueous solutions was used for interpreting how the conductivities of constituent phases influence the relaxation pattern.

RELATIONSHIP BETWEEN DIELECTRIC RELAXATION AND THE NUMBER OF INTERFACES

Theoretical analysis: The triphase system with different electric properties in the stratified structure which is schematically shown in Fig. 1(A) may be considered to be equivalent to the combination shown in Fig. 1(B). From a dielectric point of view, this system can be represented by a series combination of three sets of lumped capacitances and conductances as illustrated in Fig. 1(C), which can be measured in terms of the equivalent capacitance C and equivalent conductance G in parallel at each frequency as shown in Fig. 1(D).

The complex capacitance C^* of the whole system is represented by a relationship:

$$1/C^* = 1/C_a^* + 1/C_b^* + 1/C_f^* \tag{1}$$

where C_a^*, C_b^*, C_f^* are the complex capacitances of constituent phases a, b and f, respectively. The complex capacitances are defined by relationships

$$C^* = C + G/(2\pi f j) \tag{2}$$

(f is the frequency of the applied AC voltage, $j = \sqrt{-1}$ is the imaginary number)

after rearrangement of Eq. (1), we have

$$C = C_h + (C_l - C_m)/[1 + (f/f_p)^2] + (C_m - C_h)/[1 + (f/f_q)^2] \qquad (3)$$

$$G = G_l + [(G_m - G_l)(f/f_p)^2]/[1 + (f/f_p)^2] + [(G_m - G_h)(f/f_q)^2]/[1 + (f/f_q)^2] \qquad (4)$$

where the quantities C_l, G_l, C_h and G_h are the limiting values of the C and G at low (subscript "l") and high (subscript "h") frequencies, respectively. The C_m and G_m are the capacitance and conductance at intermediate frequencies, and f_p and f_q are the relaxation frequencies. The capacitances C_l, C_m, C_h, the conductances G_l, G_m, G_h and the relaxation frequencies f_p, f_q can be obtained from the dielectric spectroscopy as will be seen in the next section, and are represented by the use of the phase parameters C_a, C_b, C_f, G_a, G_b and G_f in a complicated form[9].

From Eqs. (3) and (4), it is seen that the series combination of three phases gives rise to two dielectric relaxations, $(C_l - C_m)/[1 + (f/f_p)^2]$ and $(C_m - C_h)/[1 + (f/f_q)^2]$, which are characterized by two relaxation frequencies, f_p and f_q, except for the case[3] $C_a/G_a = C_b/G_b = C_f/G_f$.

In order to confirm the relationship between dielectric relaxation and the interfaces in number and facilitate the understanding of this relationship, a numerical calculation was carried out with the following sets of phase parameters: $C_a = 30$ pF, $C_b = 40$ pF, $C_f = 500$ pF; $G_a = 20$ μS, $G_b = 5$ μS, $G_f = 25$ μS, which are approximately actualized in the system of film immersed in solutions. The frequency dependence of $C(f)$ and $G(f)$ was calculated by means of
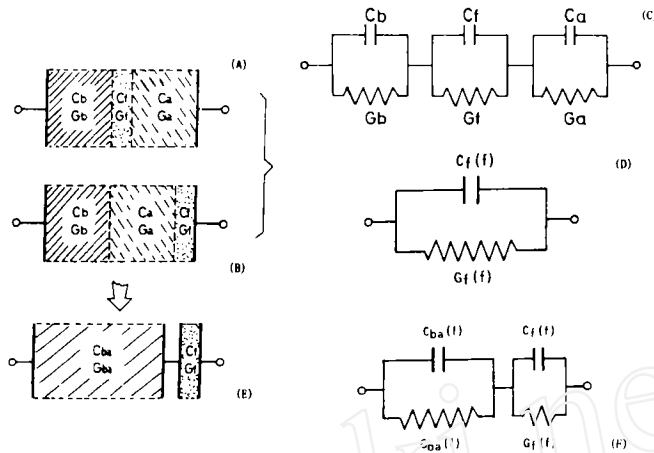

Fig. 1 (A), (B): Schematic representation of a triphase system composed of a film separating two electrolyte solutions of different concentrations. (C): Circuit model of the system shown in Fig. 1(A), (B). (D): Apparent capacitance C (f) and conductance G (f) of the whole system. (E): Series combination of composite phase ba and film phase f. (F): Equivalent circuit model of the combination shown in Fig. 1(E).
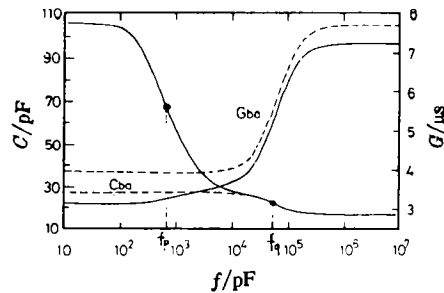

Fig. 2 Frequency dependence of the capacitance C and conductance G for the system in planer structures shown Fig. 1. The solid lines and the dashed liner are calculated from Eq. (1)(solid lines) and Eq. (5)(dashed lines) based on the model Fig. 1(A) and Fig. 1(E), respectively.

Eqs. (1) to (4), and the results are shown in Fig. 2.

The results (solid curves) demonstrate a couple of dielectric relaxation, termed P-relaxation for lower frequencies and Q-relaxation for higher frequencies. The two dielectric relaxations can be considered to be due to the existence of the three phases with different electrical properties, a, b and f, or two interfaces for the present chosen system. Furthermore, phase f can be separated from the triphase system from the dielectric point of view, and the equivalent circuit models are shown in Fig. 1(F). Hence the following simplified analysis is admissible. The system with three phase structure in Fig. 1(A) and (B) is understood to be a series combination of two phases: one is f phase, the other being a composite phase (termed ba) of b and a as illustrated in Fig. 1(E). According to the Eq. (1), the complex capacitance $C_{ba}{}^{*}$ of the composite phase ba can be expressed as

$$1/C_{ba}^{*} = 1/C_a^{*} + 1/C_b^{*} = 1/C^{*} - 1/C_f^{*} \qquad (5)$$

The system comprising the phase a and the phase b is a heterogeneous system containing one interface. As a general rule, such a system shows one dielectric relaxation undoubtedly confirmed by the results of simulation shown in Fig. 2 (dashed line). On the analogy of the case of three phases discussed above, the frequency dependence of C_{ba} and G_{ba} shows only one dielectric relaxation can also be considered to be the relaxation of interfacial polarization.

From the above analysis, it can be seen that the number of dielectric relaxations are associated with the number of the constituent phases. Diphase systems are characterized by only one relaxation frequency, whereas triphase systems require two relaxation frequencies for a complete description of the dielectric properties. The analysis presented above can be extended to multiphase systems. However, the mathematical treatment becomes increasingly cumbersome as the number of constituent phases increase.

Confirmation of a practical example: No practical examples of tetraphases systems and pentaphase systems either in planar or spherical structure have been observed so far. A simple example of triphase systems in planar structure is a composite system of a Teflon film sandwiched between two aqueous electrolyte phases with different concentrations as shown in Fig. 3(B)[10]. A parallel-plate capacitor type cell for dielectric measurements was employed and have been described in previous papers[8,10]. Measurements of capacitance and conductance were carried out with YHP 4192A LF-Impedance Analyzer from which acquired data was transferred to a computer (NEC PC-9801) for further processing. The stray capacitance and residual inductance arising from the cell assembly were compensated by an internal function of the analyzer.

The two side compartments of Fig. 3(A) are filled with 1 mmol/L KCl solutions to carry out the first series of observations. The frequency profile of capacitance C and conductance G of this composite system is shown with closed circles (●) in Fig. 3(A), exhibiting one dielectric relaxation termed Q-relaxation at higher frequencies. The Q-relaxation is characterized by relaxation frequencies fq corresponding to $(C_l + C_h)/2$ for 1 and 0.3 mmol/L KCl and to $(C_m + C_h)/2$ for 0.1, 0.5 mmol/L KCl and distilled water (D. W.). When the left side is changed from 1 mmol/L to 0.3, 0.1, 0.05

mmol/L KCl and finally with D. W. respectively, the results are shown with corresponding hollow circles (○) in Fig. 3 (A). The Q-relaxation is remains unchanged except for the case of 0.1, 0.3 mmol/L KCl, whereas a new relaxation can be observed at lower frequency side termed P-relaxation characterized by f_p corresponding to $(C_i + C_m)/2$. The intensity $(\Delta C = C_m - C_i$ or $C_l - C_m)$ of the relaxation is almost independent of KCl concentrations and the relaxation frequency f_p shifts to lower frequencies with the decrease in the KCl concentration in the left side. That is, the one-relaxation profile is changed into a two-relaxation pattern when the two compartments are filled with KCl solutions of different concentrations.

The value of relaxation frequency f_p linearly depends on the value of conductances which is in proportion to the conductivity in the left side of the film as shown in Fig. 4 (curve a). This result suggests that the mechanism of relaxation may be related to the behavior of mobile charges. The mobility of charge carriers, the ions, migrating in this heterogeneous system can be significantly higher in the aqueous phase compared with the film phase. This inevitably leads to a build up of the ions at non-conducting boundaries and results in a non-uniform charge distribution in this region, which is so-called interfacial polarization.

The two-step relaxation is attributed to interfacial polarization at two kinds of boundaries between the film and the aqueous phases, which are 0.3 mmol/L KCl solution (or 0.1, 0.05 mmol/L KCl, D. W.) and 1
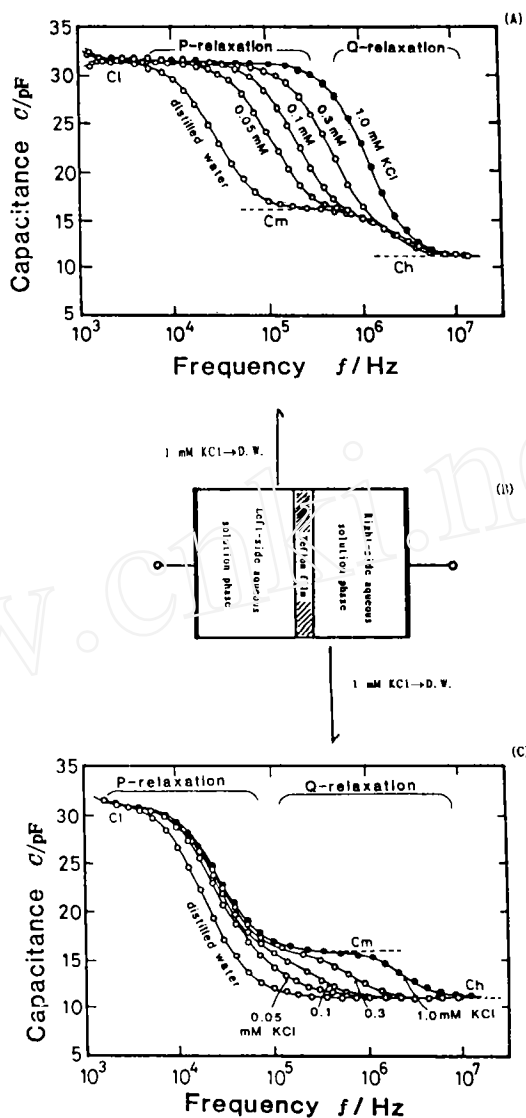

Fig. 3　(A): Series combination of a left side aqueous solution, a Teflon film and a right side aqueous solution. (B): Frequency dependence of the C for the case in which the left side compartment is D. W., and right side is filled with different concentrations of KCl solution. (C): Frequency dependence of the C for the case in which the right side is 1 mmol/L KCl and the concentration of KCl solution of left side is changed.

mmol/L KCl for the two sides of the film respectively.

　　Another series of observations were carried out that the left side compartment is filled with D. W. and the right side is first filled with 1 mmol/L KCl solution and then refilled with 0. 3, 0. 1, 0. 05 m mol/L KCl and finally with D. W. respectively. The results are shown in Fig. 3(C), the two-relaxation profile degenerates into one-relaxation when the both compartments are filled with the same kind of D. W.. Similarly, the relaxation frequency f_q shifts markedly to lower frequencies with decreasing KCl concentration in right side of the film, this dependence is also shown in Fig. 4(curve b).

　　In short, the two-relaxation profile degenerates into a one-relaxation pattern when both sides of the Teflon film are brought to the same kind of interfaces with respect to the constituent phase.

　　From Fig. 3(B) and (C), it can be seen that when the concentration of KCl solution is increased, the dielectric relaxations shift to the higher frequency side. The dielectric relaxation of this sort is interpreted as the relaxation of the interfacial polarization. At frequencies lower than the characteristic frequencies f_q, mobile ions in the aqueous phase are moved towards and accumulated at

Fig. 4　Dependence of the relaxation frequencies fp and fq on the conductivity of the aqueous solution phases

the interfaces of different phases, where the intense electric polarization is effected. On the contrary, at frequencies higher than the f_q, the interfacial polarization can not be formed because of lack of time enough for the ion migration, exhibiting small value of capacitance. This frequency dependence of the heterogeneous systems are different from both of the individual constituent phases which can be considered to be homogeneous systems.

CONCLUDING REMARKS

　　From the theoretical analysis and practical example given above, it is concluded that the dielectric relaxations observed for the film-solution system are attributed to their heterogeneous structures and can be interpreted as interfacial polarization. The number of dielectric relaxations for the heterogeneous systems with planar structure are equal to that of the kinds of interfaces contained in the systems. The intensity of the dielectric relaxation and characteristic frequencies are strongly related to the structure and the electrical properties of the constituent phases. The dielectric analysis for such systems is effective for obtaining the interior information without disturbing the specimens. The results of the theoretical analysis are shown to be in agreement with that observed experimentally in the feature of dielectric relaxation.

　　It should be noted that in the theoretical analysis part of the text, although a model of solution/film was used, no limitations if the constituent phases were solid or liquid were given. Hence the
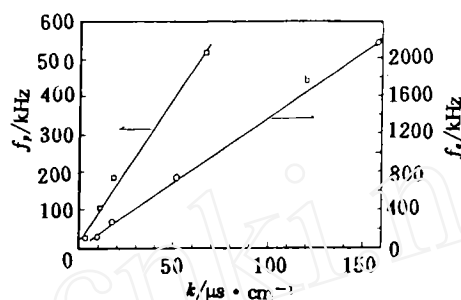
conclusions suit all of the heterogeneous systems in which the constituent phases can be solid and liquid. In other words, the systems can include solid/liquid, solid/solid and liquid/liquid interfaces, but not electrode/solid or electrode/liquid interfaces which is an intricate problem, being outside the present work.

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