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Low Frequency Dielectric Relaxations of Cellulose Acetate Membranes in Aqueous Electrolyte Solutions

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Dielectric behaviour was studied of cellulose acetate (CA) membranes with different degrees of acetyl substitution in aqueous electrolyte solutions. A dielectric relaxation was observed, being represented by the circular arc rule. The limiting value of the relative permittivity of the membrane at high frequencies ε_{fh} is proportional to the water contents of the CA membranes. The limiting value of the relative permittivity of the membrane at low frequencies ε_{fl} is increased with the increase in the value of PH, salt concentration and surfactant concentration of the ambient aqueous solution, while the value of ε_{fh} is unchanged. The relaxation frequency f_0 linearly depends on the value of the ionic conductivity κ_{fl} of the membrane. On the basis of the results mentioned above, the mechanism of the dielectric relaxation was discussed in the light of the theory of the interfacial polarization.

KEY WORDS: Dielectric relaxation/ Interfacial polarization/ Cellulose acetate membrane

1. INTRODUCTION

For a system composed of some phases, the dielectric relaxations due to the interfacial polarization are observed. In order to study the heterogeneous structure of polymer solids, the dielectric observations of polymer solids were reported by several authors[1~5]. They exhibited that the low frequency dielectric relaxation was observed and the theories of the dielectric relaxation due to the interfacial polarization were capable of being applied to the description of the relaxation.

In a previous paper, the dielectric properties of cellulose acetate (CA) membranes in aqueous solution - the different experimental system of the studies mentioned above - were reported[6]. It was found that the low frequency relaxation was observed for the cellulose acetate membranes in aqueous solution. This paper presents the report of the characteristics of the low frequency relaxation of the CA membranes in aqueous solutions and the discussion of the mechanism of the relaxation in the light of the theory of the interfacial polarization, for the purpose of obtaining information on the heterogeneous structure of the CA membrane in aqueous solution.

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2. EXPERIMENTAL

2.1 *Preparation of Membranes*

The membranes used in this work were prepared from cellulose acetates with different degrees of acetyl substitution, the specimens being kindly supplied by Daicel Co. Ltd. except for the 39.8% acetylated one (Eastman Codak 398-3). The membrane was obtained by casting the CA solution on a flat glass plate floated on mercury and evaporating the solvent completely. The acetyl contents, the degree of acetyl substitution (DS) and the solvents used for preparing the casting solutions are summarized in Table 1.

Table 1. The degree of substitution (DS), the acetyl contents of the cellulose acetates and the solvents used for preparing the casting solutions.

DS	Acetyl content (%)	solvent used
1.72	31.6	acetone/methanol (3/2)
2.13	36.4	acetone
2.25	37.7	acetone
2.30	38.2	acetone
2.38	39.2	acetone
2.45	39.8	acetone
2.88	43.8	methylene chloride/methanol (9/1)

2.2 *Dielectric Measurements*

The dielectric measurements were carried out with Yokogawa Hewlett Packard

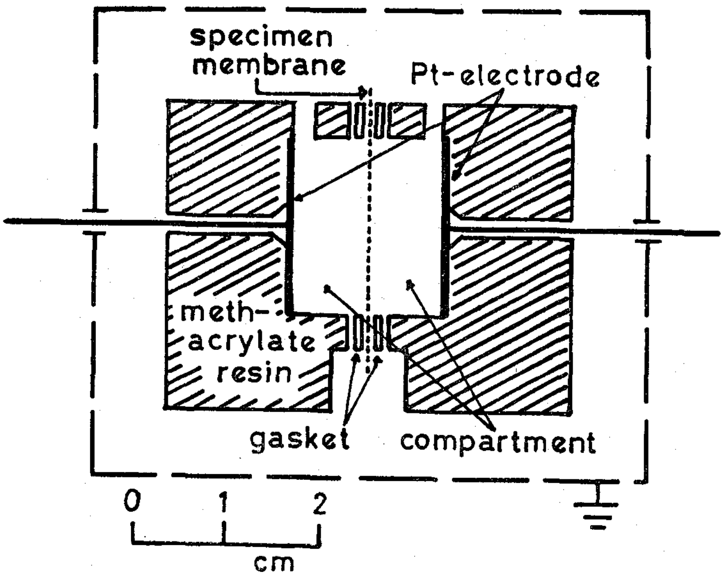

Fig. 1. Measuring cell system for the dielectric measurements of the membrane immersed in an aqueous solution.

4192A LF Impedance Analyzer operating in a frequency range of 5Hz to 13 MHz. The measuring cell system is shown in Fig. 1. All measurements were carried out at 25°C.

3. RESULTS AND DISCUSSION

3.1 *Dependence of the Degree of Acetyl Substitution (DS) of the CA Membranes*

Figure 2 shows the frequency dependence of the capacitance C and the conductance G observed for the cell systems composed of the CA membrane and the compartments filled with a 20 mM NaCl solution. Figure 3 shows the complex plane plots of the same data. Two dielectric relaxations were observed clearly.

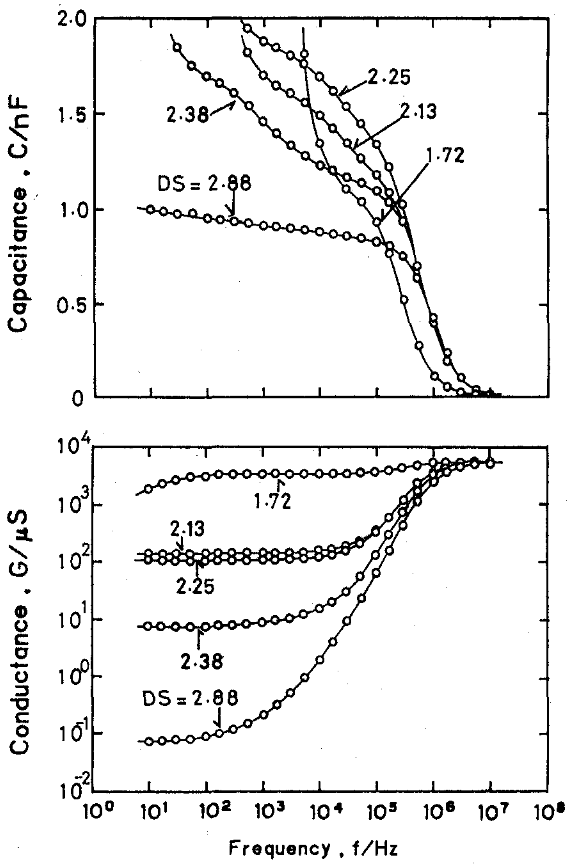

Fig. 2. Frequency dependence of the capacitance C and the conductance G observed for the cell systems composed of the CA membranes separating a 20 mM NaCl solution.

The dielectric relaxation at higher frequencies may be due to the polarization at the interfaces between membrane and aqueous solution. Hence, the complex capacitance of the CA membrane in aqueous solution C_f^* is found to be calculated by substituting the complex capacitance of aqueous solutions C_w^*, using the following equation[6]:

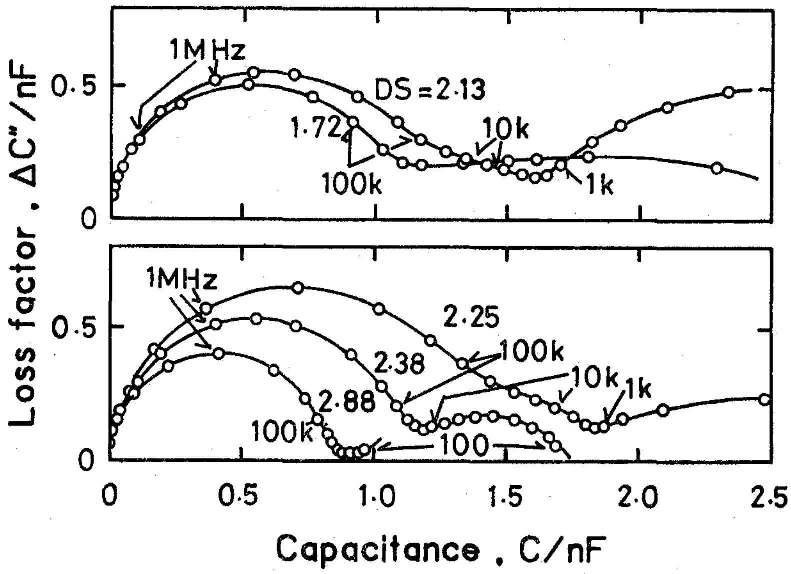

Fig. 3. Complex plane plots of the complex capacitance of the same data as shown in Fig. 2.

$$\frac{1}{C_f^*}=\frac{1}{C^*}-\frac{1}{C_w^*}, \tag{1}$$

$$C^*=C+\frac{G}{jw}, \tag{2}$$

Where ω is the angular frequency and j is the imaginary unit. The relative permittivity ε_f and conductivity κ_f of the CA memberane are calculated by use of the following equations at each frequency:

$$\varepsilon_f=\frac{C_f t}{\epsilon_v S}, \tag{3}$$

$$\kappa_f=\frac{G_f t}{S}, \tag{4}$$

where t is the thickness of the membrane, S is the membrane area and ϵ_v is the permittivity of vacuum.

Figure 4 shows the frequency dependence of ε_f, κ_f of the CA membranes in 20 mM NaCl solution. A dielectric relaxation was observed, being represented by the circular arc rule of the following[7]:

$$\varepsilon_f=\varepsilon_{fh}+\frac{(\varepsilon_{fl}-\varepsilon_{fh})\left[1+(f/f_0)^{\beta}\cos\left(\frac{\pi}{2}\beta\right)\right]}{1+2(f/f_0)^{\beta}\cos\left(\frac{\pi}{2}\beta\right)+(f/f_0)^{2\beta}}, \tag{5}$$

$$\kappa_f=\kappa_{fl}+\frac{w\epsilon_v(\varepsilon_{fl}-\varepsilon_{fh})\,(f/f_0)^{\beta}\sin\left(\frac{\pi}{2}\beta\right)}{1+2(f/f_0)^{\beta}\cos\left(\frac{\pi}{2}\beta\right)+(f/f_0)^{2\beta}}, \tag{6}$$

where ε_{fl}, ε_{fh} are the limiting values of the relative permittivity ε_f at low and high frequencies respectively, κ_{fl} the limiting value of κ_f at low frequencies, f_0 the

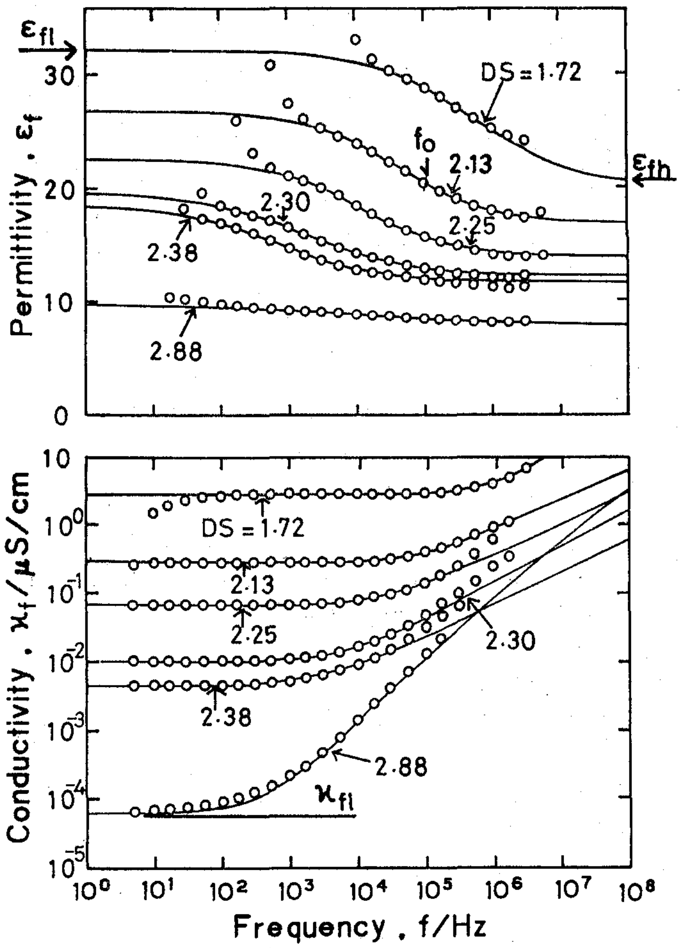

Fig. 4. Frequency dependence of the relative permittivity ε_f and the conductivity κ_f of the CA membranes in a 20 mM NaCl solution. The curves are the values calculated by Eq. 5 and Eq. 6.

relaxation frequency and β the distribution coefficient of the relaxation times. By use of the least square method, the data were fitted to Eq.5, as shown by the theoretical curves in Fig. 4. The complex plane plots of the complex relative permittivity of the same data are shown in Fig. 5. The parameters obtained are summarized in Table 2, together with the water content of the membrane H, the membrane thickness t and the relative permittivity of the completely dried CA membrane ε_{fd} obtained by the separate dielectric measurements.

The paramatars obtained for the 43.8% acetylated one (DS=2.88) may be the values for the dielectric relaxation caused by the different origin. The similar relaxation was observed for the completely dried membranes. It may be attributed to the movement of the side chains[8], but being out of the further discussion in this paper. The low frequency relaxation was observed for the 43.8% acetylated one in a frequency range below 50 Hz as shown in Fig. 4.

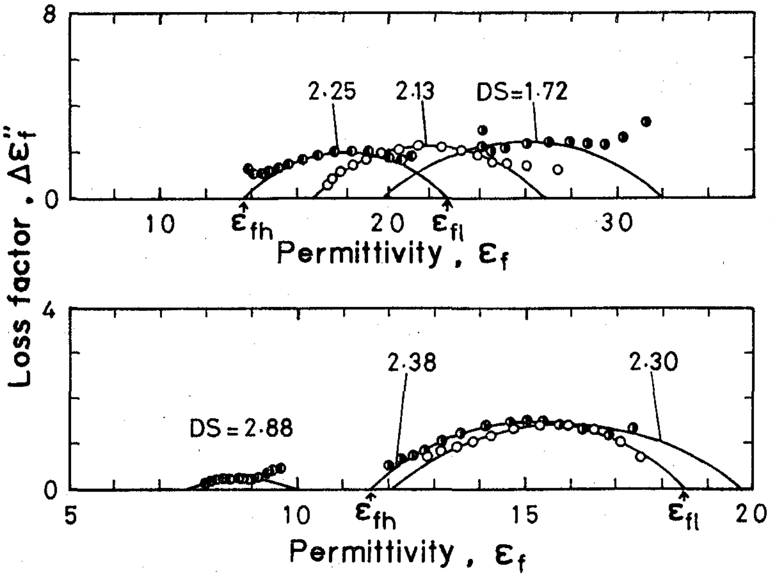

Fig. 5. Complex plane plots of the complex relative permittivity of the same data as shown in Fig. 4. The curves are the value calculated by Eq. 5 and Eq. 6.

Table 2. Dielectric parameters obtained for the cellulose acetate membranes in 20 mM NaCl solution, and the thickness t, the water content H and the relative permittivity of the completely dried membrane ε_{fd}.

DS	t / μm	ε_{fl}	ε_{fh}	κ_{fl} / $\mu S\ cm^{-1}$	f_0 / kHz	β	ε_{fd}	H / %
1.72	9.2	36.5	20.6	2.30	342	0.43		26.8
	9.9	36.2	14.1	2.14	1080	0.35		24.9
	11.4	33.0	21.1	3.16	383	0.49	5.1	25.0
	28.1	32.2	19.8	2.76	567	0.49	5.8	26.4
2.13	25.6	26.2	16.7	2.99×10^{-1}	40.2	0.60		20.7
	33.1	26.8	16.8	2.86×10^{-1}	41.6	0.53	4.6	19.5
	41.7	28.5	15.9	2.02×10^{-1}	21.3	0.49		20.4
2.25	8.0	23.6	13.6	3.66×10^{-2}	5.26	0.58		
	16.6	22.6	13.8	6.87×10^{-2}	11.9	0.53	4.3	15.5
	25.8	23.0	13.5	3.44×10^{-2}	5.40	0.58	4.4	16.4
	32.4	23.6	14.8	1.14×10^{-1}	26.0	0.57		19.5
2.30	7.1	19.2	11.6	8.90×10^{-3}	1.70	0.49		
	10.9	19.7	12.0	1.04×10^{-2}	1.76	0.46	4.2	
2.38	7.8	18.4	11.2	1.83×10^{-3}	0.268	0.43		
	11.2	18.6	11.6	4.61×10^{-3}	0.715	0.51	4.3	
	26.8	16.4	11.6	7.10×10^{-3}	1.65	0.47	4.4	14.0
	31.9	21.4	12.5	8.14×10^{-3}	0.916	0.52		16.4
2.88	10.1	10.0	7.7	6.43×10^{-5}	7.81	0.26		10.5
	15.8	9.8	6.9	5.33×10^{-5}	5.15	0.21	3.9	9.0
	16.2	11.9	6.9	9.96×10^{-4}	582	0.18		11.8
	22.4	10.9	8.9	1.14×10^{-4}	10.5	0.39		12.4
	26.9	9.2	7.4	6.25×10^{-5}	48.2	0.31	3.5	10.7

The whole behaviour of this relaxation was, however, not observed because of the low frequency limitation for the measurements of our instruments. Hence, the parameters for the 43.8% acetylated one will not be discussed, except for the limiting value of the relative permittivity at low frequencies ε_{fl}. The value of ε_{fl} for the 43.8% acetylated one may be considered to be the limiting value of the relative permittivity at high frequencies for the low frequency relaxation, i.e., the value ε_{fh} of the other data.

Figure 6 shows the plots of ε_{fl}, ε_{fh}, ε_{fd} against the value of DS. The values of ε_{fl}, ε_{fh} are increased with the decrease in the value of DS, while ε_{fd} is almost unchanged. The value of the water content H increases with the decrease in the value of DS as summarized in Table 2. The relative permittivities ε_{fl}, ε_{fh} may be related to the water content H.

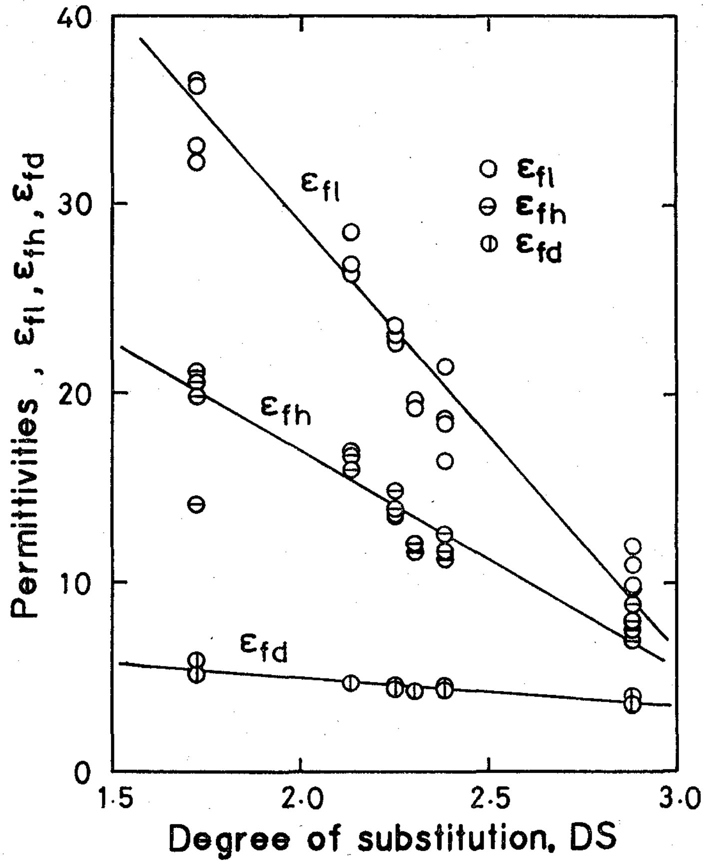

Fig. 6. Dependence of the relative permittivities ε_{fl} ε_{fh}, ε_{fd} on the value of DS of the CA membranes.

The value of the relaxation frequency f_0 linearly depends on the value of κ_{fl} as shown in Fig. 7. It is given by the relation: $f_0=\kappa_{fl}/(2\pi\epsilon_v\varepsilon_{fh})$. This result suggests that the mechanism of the relaxation may be related to the behaviour of mobile charges.

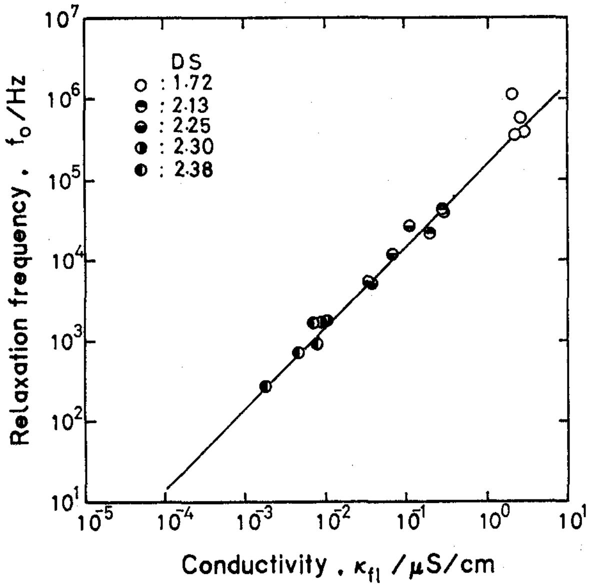

Fig. 7. Dependence of the relaxation frequency f_0 on the conductivity κ_{fl} of the CA membranes immersed in a 20 mM NaCl solution.

3.2 *Dependence on the Salt Concentration and Salt Species*

In order to obtain the more information of the characteristics of the low frequency relaxation, dielectric observations of the CA membrane in aqueous solution were further extended to the cases of the different concentrations and types of salts. The parameters obtained by the same analysis as mentioned in Section 3.1 are summarized in Tables 3 and 4.

Figure 8 shows the dependence of the values of ε_{fl}, ε_{fh} on the NaCl concentration C_s of the ambient aqueous solution at PH=6. The value of ε_{fl} is increased with the increase in the value of C_s, while the value of ε_{fh} is unchanged. The similar dependence can be seen from the data of other PH values and different kinds of salts (Tables 3 and 4). Hence, the limiting value of the relative permittivity at high frequencies ε_{fh} may be given as a function of the ralative permittivity of the completely dried membrane ε_{fd}, the water content H and the relative permittivity of water ε_w. This will be discussed later.

The value of the relaxation frequency f_0 linearly depends on the value of κ_{fl} as shown in Figs. 9 and 10. It is also given by the relation: $f_0=\kappa_{fl}/2\pi\epsilon_v\varepsilon_{fh}$. The conductivity κ_{fl} can be understood to the ionic conductivity in direct current. The dependence of κ_{fl} on the salt concentration shows that the CA membranes are weakly charged[6]. The values of κ_{fl} in the results of the different kinds of salts (Table 4) show the ionic selectivity of the CA membrane. The values of κ_{fl} in Table 4 increase in the order:

divalent cation $<$ univalent cation

and

$SO_4^{--} < F^- < Cl^- < Br^- < I^- < NO_3^-$.

Table 3. Dielectric parameters obtained for the cellulose acetate membranes in the NaCl solutions of different concentrations and different PH values.

DS	NaCl Conc.	PH	ε_{fl}	ε_{fh}	$\frac{\kappa_{fl}}{\mu S\ cm^{-1}}$	$\frac{f_0}{Hz}$	β
2.13	1 mM	6	23.8	17.6	0.181	4.68×10^4	0.66
	10 mM	3	23.4	16.3	1.36	8.40×10^4	0.44
	10 mM	4	24.0	16.7	0.256	3.83×10^4	0.53
	10 mM	5	25.3	16.9	0.231	5.14×10^4	0.56
	10 mM	6	26.0	17.3	0.268	5.93×10^4	0.60
	100 mM	3	31.3	16.6	2.04	1.38×10^5	0.53
	100 mM	4	31.5	15.9	1.36	1.21×10^5	0.50
	100 mM	5	33.7	16.5	1.32	9.28×10^4	0.50
	100 mM	6	36.9	15.7	1.51	8.69×10^4	0.45
2.25	1 mM	6	22.0	15.3	6.59×10^{-2}	1.69×10^4	0.62
	10 mM	3	20.9	14.6	0.488	3.51×10^4	0.46
	10 mM	4	21.5	15.0	8.06×10^{-2}	1.14×10^4	0.54
	10 mM	5	23.3	15.3	6.99×10^{-2}	1.69×10^4	0.55
	10 mM	6	24.8	15.4	0.102	2.51×10^4	0.58
	100 mM	3	28.7	14.5	0.615	3.93×10^4	0.49
	100 mM	4	28.3	14.9	0.384	3.45×10^4	0.53
	100 mM	5	30.1	14.4	0.363	2.80×10^4	0.48
	100 mM	6	33.0	14.8	0.434	2.99×10^4	0.48
2.38	1 mM	6	16.8	12.9	4.82×10^{-4}	94.3	0.52
	10 mM	3	18.2	12.3	5.44×10^{-3}	5.95×10^2	0.54
	10 mM	4	17.7	12.5	1.31×10^{-3}	1.28×10^2	0.52
	10 mM	5	17.8	12.8	8.00×10^{-4}	83.3	0.51
	10 mM	6	17.4	13.2	9.84×10^{-4}	2.21×10^2	0.62
	100 mM	3	20.1	12.1	1.41×10^{-2}	1.82×10^3	0.53
	100 mM	4	20.1	12.3	8.37×10^{-3}	1.40×10^3	0.54
	100 mM	5	20.2	12.3	7.63×10^{-3}	1.26×10^3	0.54
	100 mM	6	20.8	12.4	7.64×10^{-3}	1.16×10^3	0.53
2.45	1 mM	6	19.5	12.8	2.57×10^{-3}	4.26×10^2	0.63
	10 mM	3	17.0	11.8	4.30×10^{-2}	5.41×10^3	0.51
	10 mM	4	19.6	12.6	5.37×10^{-3}	3.67×10^2	0.55
	10 mM	5	20.8	12.9	2.86×10^{-3}	3.34×10^2	0.58
	10 mM	6	21.7	13.4	3.36×10^{-3}	4.53×10^2	0.63
	100 mM	3	26.1	12.3	3.23×10^{-2}	1.57×10^3	0.54
	100 mM	4	26.3	12.6	1.41×10^{-2}	1.27×10^3	0.58
	100 mM	5	27.1	12.8	1.34×10^{-2}	1.22×10^3	0.58
	100 mM	6	27.7	12.8	1.50×10^{-2}	1.29×10^3	0.57

This is considered to be the sequence of permeating the CA membrane with more easy, being the same order of the reverse osmosis experiments of CA membranes by other authors.

3.3 *The Effect of the Surfactants*

In order to study the effect of the ion adsorption on the relaxation, the dielectric observations were carried out for the cell systems composed of the CA membrane and the compartments filled with the 20 mM NaCl solution containing surfactants. The results are summarized in Table 5.

Table 4. Dielectric parameters obtained for the 39.2% acetylated cellulose acetate membrane in the different types of salt solutions of concentration 0.02 eq./l.

Salt	ε_{fl}	ε_{fh}	$\frac{\kappa_{fl}}{\mu S\ cm^{-1}}$	$\frac{f_0}{Hz}$	β
LiCl	17.1	11.4	7.57×10^{-4}	62.9	0.41
NaCl	17.3	11.4	1.83×10^{-3}	372	0.45
KCl	17.0	11.2	1.74×10^{-3}	240	0.45
RbCl	17.4	11.5	1.76×10^{-3}	200	0.46
CsCl	17.5	11.4	1.53×10^{-3}	176	0.45
NH_4Cl	17.5	11.2	2.46×10^{-3}	302	0.41
$CaCl_2$	14.2	12.0	5.51×10^{-4}	73.5	0.73
$MgCl_2$	16.1	11.9	6.40×10^{-4}	23.9	0.46
$SrCl_2$	14.5	11.8	5.59×10^{-4}	57.2	0.60
$LaCl_3$	14.3	11.6	7.21×10^{-4}	74.6	0.60
$CeCl_3$	16.2	11.4	8.02×10^{-4}	13.5	0.43
NaF	17.6	11.4	1.15×10^{-3}	219	0.42
NaBr	17.9	11.4	2.36×10^{-3}	281	0.45
NaI	19.8	11.7	3.91×10^{-3}	643	0.52
$NaNO_3$	17.0	11.2	6.56×10^{-3}	1.07×10^{3}	0.50
Na_2SO_4	16.0	12.1	5.77×10^{-4}	95.2	0.58

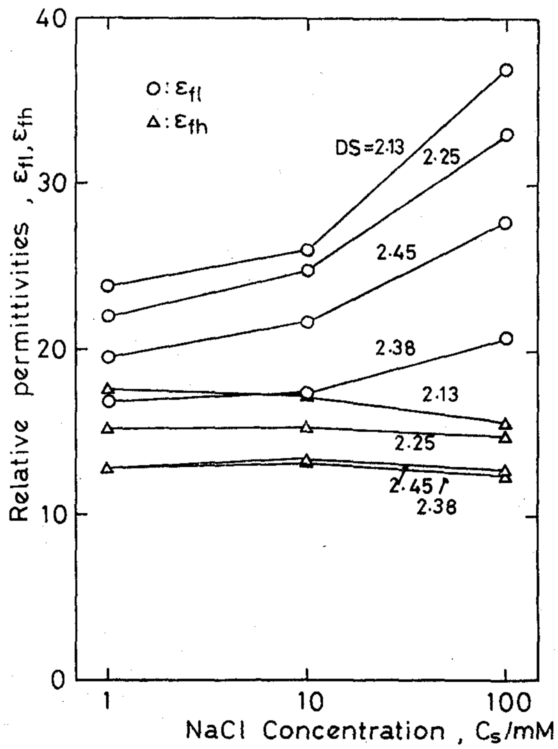

Fig. 8. NaCl concentration dependence of the relative permittivities ε_{fl}, ε_{fh}.

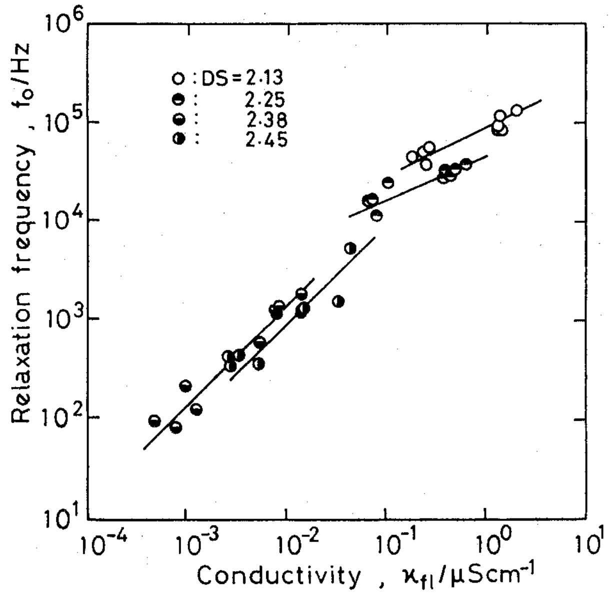

Fig. 9. Dependence of the relaxation frequency f_0 on the conductivity κ_{fl} of the CA membranes immersed in NaCl solutions of different concentrations.

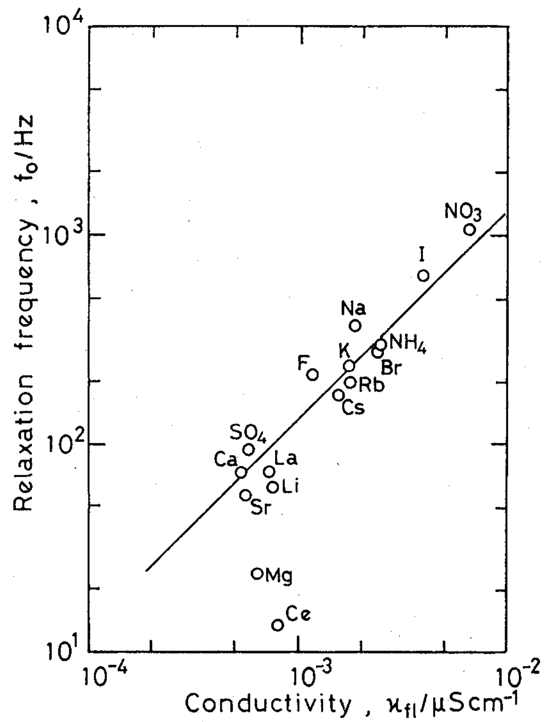

Fig. 10. Dependence of the relaxation frequency f_0 on the conductvity κ_{fl} of the CA membrane immersed in diifferent types of salt solutions of concentration 0.02 eq./l.

Table 5. Dielectric parameters obtained for the cellulose acetate membranes in the 20 mM NaCl solutions containing surfactants. The surfactants used are Cetyltrimethylammonium Chloride (CE) and Sodium Laurylsulfate (SDS).

DS	surfactants	Conc.	ε_{fl}	ε_{fh}	$\frac{\kappa_{fl}}{\mu S\ cm^{-1}}$	$\frac{f_0}{Hz}$	β
2.45	SDS	0 mM	28.8	13.7	1.45×10^{-2}	8.36×10^{2}	0.53
		0.1 mM	31.6	13.5	2.57×10^{-2}	1.69×10^{3}	0.55
		0.2 mM	34.1	13.6	3.17×10^{-2}	1.91×10^{3}	0.54
		0.3 mM	34.3	14.1	3.90×10^{-2}	2.51×10^{3}	0.57
		0.5 mM	36.1	14.1	5.78×10^{-2}	3.07×10^{3}	0.57
2.45	CE	0 mM	37.8	14.8	4.80×10^{-2}	2.40×10^{3}	0.58
		0.1 mM	49.9	14.9	0.183	6.58×10^{3}	0.59
		0.2 mM	47.5	14.4	0.335	1.21×10^{4}	0.57
		0.3 mM	47.1	14.9	0.551	2.03×10^{4}	0.59
		0.5 mM	48.1	15.8	0.746	2.66×10^{4}	0.60
2.38	SDS	0 mM	20.6	12.9	3.94×10^{-3}	5.30×10^{2}	0.51
		0.1 mM	21.1	12.4	4.07×10^{-3}	6.21×10^{2}	0.50
		0.2 mM	21.9	12.7	4.35×10^{-3}	7.01×10^{2}	0.55
		0.3 mM	22.6	12.5	6.90×10^{-3}	1.19×10^{3}	0.54
		0.5 mM	23.1	12.5	9.47×10^{-3}	1.62×10^{3}	0.58
2.38	CE	0 mM	18.7	12.4	2.77×10^{-3}	4.51×10^{2}	0.48
		0.1 mM	22.7	12.3	5.15×10^{-3}	1.15×10^{3}	0.58
		0.2 mM	25.6	12.2	5.84×10^{-3}	1.24×10^{3}	0.59
		0.3 mM	28.9	12.7	6.24×10^{-3}	1.14×10^{3}	0.62
		0.5 mM	30.6	12.9	9.83×10^{-3}	1.33×10^{3}	0.66

Figure 11 shows the plots of the values of ε_{fl}, ε_{fh} against the values of the concentration of the surfactants. The same dependence was observed as that on the concentration of salts. The value of ε_{fl} is markedly increased with the increase in the value of the concentration of surfactants, while the value of ε_{fh} is unchanged. The value of the relaxation frequency f_0 linearly depends on the value of κ_{fl} as shown in Fig. 12.

3.4 *Dielectric Model of the Low Frequency Relaxation*

The characteristics of the low frequency relaxation are as follows:

1) The limiting value of the relative permittivity at high frequencies ε_{fh} is increased with the increase in the value of the water contents H of the membrane. It is unchanged under the conditions of the different compositions of the electrolytes in the ambient aqueous solution.

2) The limiting value of the relative permittivity at low frequencies ε_{fl} is increased with the increase in the value of the electrolyte (except for H^+ ion) concentration of the ambient aqueous solution.

3) The value of the relaxation frequency f_0 linearly depends on the value of the ionic conductivity κ_{fl}. It is given by the relation: $f_0=\kappa_{fl}/(2\pi\epsilon_v\varepsilon_{fh})$.

4) The values of the distribution parameter of the relaxation times β are 0.4–0.6.

As already mentioned, the value of ε_{fh} may be given as a function of the water content H, the relative permittivity of the dried CA membrane ε_{fd} and the

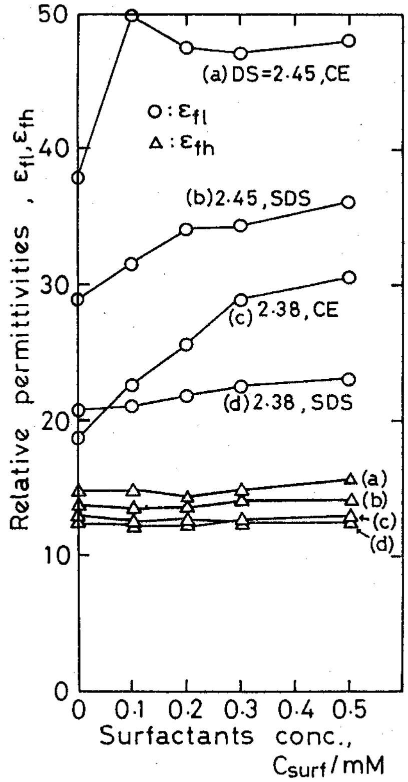

Fig. 11. Surfactants concentration dependence of the relative permittivities ε_{fl}, ε_{fh}. The surfactants used were cetyltrimethylammonium chloride (CE) and sodium laurylsulfate (SDS).

relative permittivity of water ε_w. Here, three cases of binary mixture model as shown in Fig. 13 are considered.

The case (a) is that of the molecular mixture of water and CA matrix, the relative permittivity of the whole system ε_{fh} being given by the following equation according to Onsager[9]:

$$\frac{(\varepsilon_{fh}-\varepsilon_w)(2\varepsilon_w\varepsilon_{fh}+n_w^4)}{\varepsilon_w(2\varepsilon_{fh}+n_w^2)^2}\mathrm{H}+\frac{(\varepsilon_{fh}-\varepsilon_{fd})(2\varepsilon_{fd}\varepsilon_{fh}+n_f^4)}{\varepsilon_{fd}(2\varepsilon_{fh}+n_f^2)^2}(1-\mathrm{H})=0, \qquad (7)$$

where n_f n_w are the refractive index of CA matrix and water respectively. The case (b) is that of the water pore in the CA matrix (W/O type) and (c) is that of the CA matrix in the water continuum (O/W type). The relative permittivity ε_{fh} of the cases (b), (c) is given by the following equations according to Bruggeman[10]:

$$\frac{\varepsilon_{fh}-\varepsilon_w}{\varepsilon_{fd}-\varepsilon_w}\left(\frac{\varepsilon_{fd}}{\varepsilon_{fh}}\right)^{1/3}=1-\mathrm{H}, \qquad \text{(W/O type)} \qquad (8)$$

$$\frac{\varepsilon_{fh}-\varepsilon_{fd}}{\varepsilon_w-\varepsilon_{fd}}\left(\frac{\varepsilon_w}{\varepsilon_{fh}}\right)^{1/3}=\mathrm{H}. \qquad \text{(O/W type)} \qquad (9)$$

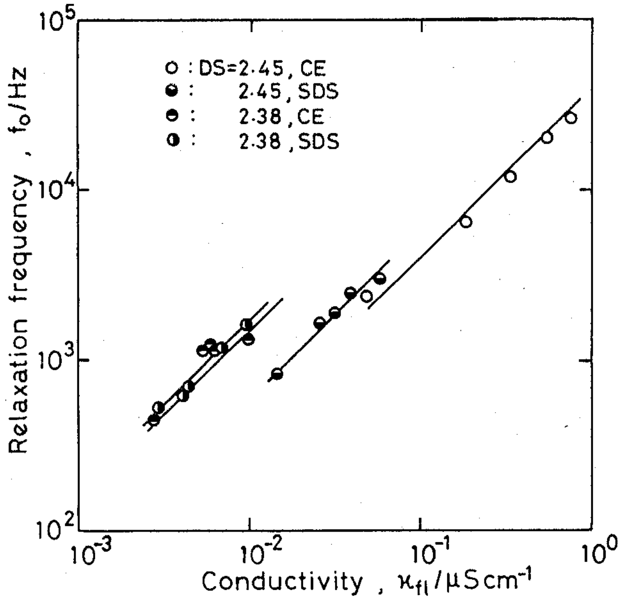

Fig. 12. Dependence of the relaxation frequency f_0 on the conductivity κ_{fl} of the CA membranes immersed in 20 mM NaCl solutions containing surfactants.

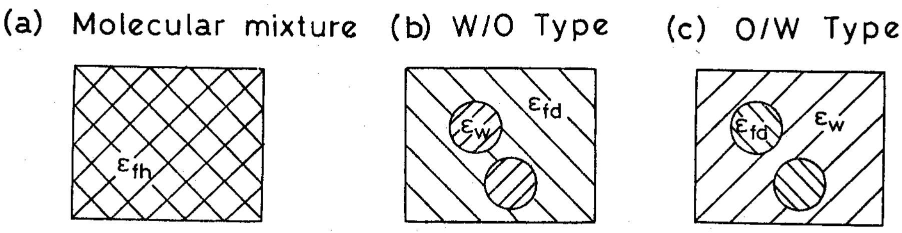

Fig. 13. Schematic presentation of the mixture model of CA matrix and water.

Figure 14 shows the curves calculated by use of Eqs. 7–9, together with the experimental values summarized in Table 2. The theoretical curves of the molecular mixture model is best fitted to the experimental points, provided that the value of the relative permittivity of water ε_w is 64. It is reasonable that the value of the relative permittivity of the adsorbed water is smaller than the value for the bulk of the water, 78[11]. Hence, the CA membrane in aqueous solution can be considered to be the homogeneous mixture of CA matrix and water. The dielectric relaxation characterized by the relaxation frequency $f_0=\kappa_{fl}/(2\pi\varepsilon_v\varepsilon_{fh})$ is, however, seen to be attributed to the interfacial polarization caused by the heterogeneous structure of the CA membrane. Hence we consider as follows.

The water distribution in the CA membrane may be a little heterogeneous, because of a little heterogeneous distribution of the degree of acetylation or carboxyl substitution or other reasons. The distribution of the value of the relative

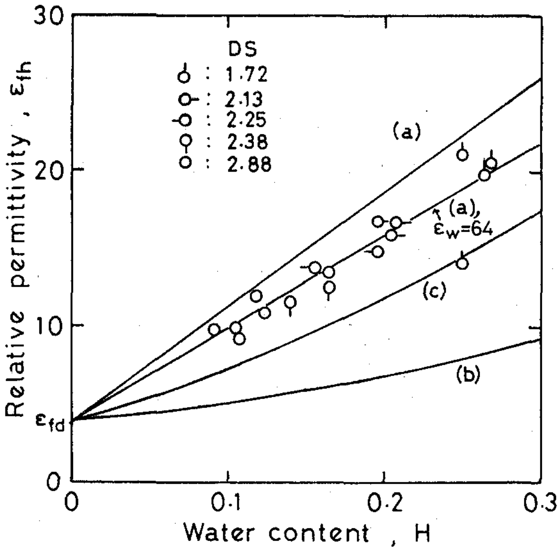

Fig. 14. Dependence of the relative permittivity ε_{fh} on the water content H. The theoretical curves are the values calculated by Eq. 7 (a), Eq. 8 (b) and Eq. 9 (c), provided that the value of ε_w is 78 instead of 64.

permittivity in the CA membrane is almost homogeneous, since the value of the relative permittivity of the CA membrane is proportional to the water content. On the contrary, the ionic conductivity depends on the water content markedly. For instance, the ionic conductivity is 100 times as large as the increase of 14% in the water content (Table 2). Hence the CA membrane in aqueous solution can be considered to be composed of various phases of almost the same value of the relative permittivity but of the different values of the ionic conductivity. In order to clarify this, the quantitative analysis is carried out for the simplest model.

For a disperse system of spherical particles with the complex permittivity ε_i^* in the continuous medium with the complex permittivity ε_a^*, Wagner proposed the following equation for the complex permittivity ε^* of the whole system[12]:

$$\varepsilon^* = \varepsilon_a^* \frac{2\varepsilon_a^* + \varepsilon_i^* - 2\Phi(\varepsilon_a^* - \varepsilon_i^*)}{2\varepsilon_a^* + \varepsilon_i^* + \Phi(\varepsilon_a^* - \varepsilon_i^*)}, \tag{10}$$

where Φ is the volume fraction of the dispersed particles and the complex permittivity is given by $\varepsilon^* = \varepsilon + \kappa/(j\omega\epsilon_v)$.

The limiting values of ε, κ at low (subscript l) and high (subscript h) frequencies and the relaxation frequency f_0 are expressed as[13]

$$\varepsilon_h = \varepsilon_a \frac{2\varepsilon_a + \varepsilon_i - 2\Phi(\varepsilon_a - \varepsilon_i)}{2\varepsilon_a + \varepsilon_i + \Phi(\varepsilon_a - \varepsilon_i)}, \tag{11}$$

$$\varepsilon_l = \varepsilon_a \frac{\kappa_l}{\kappa_a} + \frac{9(\varepsilon_i\kappa_a - \varepsilon_a\kappa_i)\kappa_a\Phi}{[2\kappa_a + \kappa_i + \Phi(\kappa_a - \kappa_i)]^2}, \tag{12}$$

$$\kappa_l = \kappa_a \frac{2\kappa_a + \kappa_i - 2\Phi(\kappa_a - \kappa_i)}{2\kappa_a + \kappa_i + \Phi(\kappa_a - \kappa_i)}, \tag{13}$$

$$\kappa_h=\kappa_a\frac{\varepsilon_h}{\varepsilon_a}+\frac{9(\kappa_i\varepsilon_a-\kappa_a\varepsilon_i)\varepsilon_a\Phi}{[2\varepsilon_a+\varepsilon_i+\Phi(\varepsilon_a-\varepsilon_i)]^2}, \tag{14}$$

$$f_0=\frac{1}{2\pi\epsilon_v}\frac{2\kappa_a+\kappa_i+\Phi(\kappa_a-\kappa_i)}{2\varepsilon_a+\varepsilon_i+\Phi(\varepsilon_a-\varepsilon_i)}. \tag{15}$$

when the value of ε_i is equal to the value of ε_a, Eqs. 11, 12, 13, 15 are

$$\varepsilon_h=\varepsilon_i=\varepsilon_a, \tag{16}$$

$$\varepsilon_l=\varepsilon_h\frac{\kappa_l}{\kappa_a}+\frac{9\varepsilon_h\kappa_a(\kappa_a-\kappa_i)\Phi}{[2\kappa_a+\kappa_i+\Phi(\kappa_a-\kappa_i)]^2}, \tag{17}$$

$$\kappa_l=\kappa_a\frac{2\kappa_a+\kappa_i-2\Phi(\kappa_a-\kappa_i)}{2\kappa_a+\kappa_i+\Phi(\kappa_a-\kappa_i)}, \tag{18}$$

$$f_0=\frac{1}{6\pi\epsilon_v\varepsilon_h}[2\kappa_a+\kappa_i+\Phi(\kappa_a-\kappa_i)]. \tag{19}$$

By means of the procedure explained in Appendix 1, the values of κ_i, κ_a, Φ are calculated from the observed values of ε_{fh}, ε_{fl}, κ_{fl}, f_0, The analysis is carried out for some cases in Table 2 and the results are listed in Table 6. The value of the ratio κ_i/κ_a is below 9. Such a little difference may occur when the water content of "i" plase is a few per cent as large as compared with that of "a" phase.

Table 6. Phase parameters calculated from the data summarized in Table 2.

DS	NaCl conc.	ε_{fl}	ε_{fh}	κ_{fl} / μS cm^{-1}	f_0 / Hz	κ_a / μS cm^{-1}	κ_i / μS cm^{-1}	Φ
1.72	20 mM	33.0	21.1	3.16	3.83×10^5	1.67	14.2	0.32
2.13	20 mM	26.8	16.8	0.286	4.16×10^4	0.146	1.24	0.34
2.25	20 mM	22.6	13.8	6.87×10^{-2}	1.19×10^4	3.41×10^{-2}	0.299	0.35
2.38	20 mM	18.6	11.6	4.61×10^{-3}	7.15×10^2	2.16×10^{-3}	1.46×10^{-2}	0.42
2.45	10 mM	21.7	13.4	3.36×10^{-3}	4.53×10^2	1.56×10^{-3}	1.09×10^{-2}	0.42

The value of the distribution parameter of the relaxation times β shows that the morphology of the heterogeneous structure of the CA membrane in aqueous solution is very complicated. Hence, the quantitative analysis of the whole relaxation behaviour is very difficult. In consideration of the dependence of the value of ε_{fl} on the concentration of salts, surfactants and H^+ ion, it is inferred that the surface charge may affect the low frequency rexalation[14].

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APPENDIX

1. Calculation of Phase Parameters κ_a, κ_i, Φ

For simplification of calculation, we put as follows:

$$2\kappa_a+\kappa_i=x, \tag{A1}$$

$$\Phi(\kappa_a-\kappa_i)=y, \tag{A2}$$

Substituting Eqs. A1, A2, Eqs. 17, 18, 19 are

$$\frac{\kappa_l}{\kappa_a}+\frac{9\kappa_a}{(x+y)^2}y=\frac{\varepsilon_l}{\varepsilon_h}, \tag{A3}$$

$$\frac{x-2y}{x+y}=\frac{\kappa_l}{\kappa_a}, \tag{A4}$$

$$x+y=6\pi\epsilon_v\varepsilon_h f_0\equiv z, \tag{A5}$$

Rearrangement of Eqs. A3, A5 with respect to x, y gives

$$y=\frac{z^2}{9\kappa_a}\left(\frac{\varepsilon_l}{\varepsilon_h}-\frac{\kappa_l}{\kappa_a}\right), \tag{A6}$$

$$x=z-\frac{z^2}{9\kappa_a}\left(\frac{\varepsilon_l}{\varepsilon_h}-\frac{\kappa_l}{\kappa_a}\right). \tag{A7}$$

Substitution of Eqs. A6, A7 into Eq. A4 and rearrangement of Eq. A4 gives

$$3\kappa_a^2-\left(z\frac{\varepsilon_l}{\varepsilon_h}+3\kappa_l\right)\kappa_a+z\kappa_l=0. \tag{A8}$$

By solving Eq. A8, we can calculate the parameter κ_a from the observed parameters ε_l, ε_h, κ_l, f_0. The parameters κ_i, Φ can be calculated from the parameters κ_a, ε_l, ε_h, κ_l, f_0, using Eqs. A1, A2, A6, A7.

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