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Piezoelectric Admittance Measurements of Montmorillonite/Poly(vinyl alcohol) Composite Film-Coated Quartz Crystal Oscillators

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The piezoelectric admittance measurements of montmorillonite/poly(vinyl alcohol) (PVA) composite film-coated quartz crystal oscillators were performed in air dried over silica gel, in an atmosphere of moisture with 100% relative humidity at 25 °C and in contact with Na_2SO_4 aqueous solutions. By use of the electrical equivalent circuit model conventionally proposed for a piezoelectric quartz crystal, the relevant circuit parameters; resistance R, inductance L, and capacitance C were evaluated as a function of the Na_2SO_4 concentration (0.01—1.0 M (1 M=1 mol dm^{-3})). R was almost constant above ca. 0.35 M and increased with decreasing the concentration in the lower concentrations, while L and C were almost independent of the concentration. On the basis of the electrolyte concentration dependence of R, the structural change of the clay/PVA composite film due to swelling with the electrolyte is discussed in comparison with the results for the clay film.

We have performed piezoelectric admittance measurements of a montmorillonite film-coated quartz crystal oscillator in contact with dry air, moisture and Na_2SO_4 aqueous media and have evaluated the relevant electrical equivalent circuit parameters, i.e., resistance R, inductance L, and capacitance C components.[1] In addition to the conventional measurement of resonant frequency, the analysis of the electrical equivalent circuit parameters of the quartz crystal oscillator provides information on the chemical and physical processes in the film matrix applied to the oscillator.[1] It has been found that the swelling behavior of the montmorillonite film is strongly affected by the electrolyte concentration. This was consistent with the results in the previous work based on other approaches such as X-ray diffraction, ESR, conductivity, and electrochemical measurements.[2-9]

The present paper discribes the piezoelectric admittance measurements of the quartz crystal oscillator coated with a montmorillonite/poly(vinyl alcohol) (PVA) composite film in contact with Na_2SO_4 aqueous solutions of various concentrations. The relevant circuit parameters have been estimated and the effect of PVA on the swelling of the clay/PVA composite film was discussed based on the circuit parameters estimated. It has been found that the introduction of PVA to the montmorillonite matrix markedly promotes the heterogeneous electron-transfer and homogeneous charge-transport kinetics at the clay/PVA film-coated electrodes.[10,11] The data obtained for the quartz coated with the clay/PVA film are discussed in comparison with the previous results[1] obtained for the quartz crystal oscillator with the montmorillonite alone as a coating film.

Experimental

Materials. A 5 MHz AT-cut quartz crystal (in 13 mm diameter, Toyo Kurafuto Co., Ltd.) was used as a piezoelectric oscillator as reported previously.[13-17] The sodium montmorillonite sample employed was from the Source Clays Repository, Department of Geology, University of Missouri.[10,11] Poly(vinyl alcohol) (PVA) (Kanto Chemical Co., M.W.=2.7×10^4) and anhydrous sodium sulfate of reagent grade (Wako Pure Chemicals Co.) were used as received. The

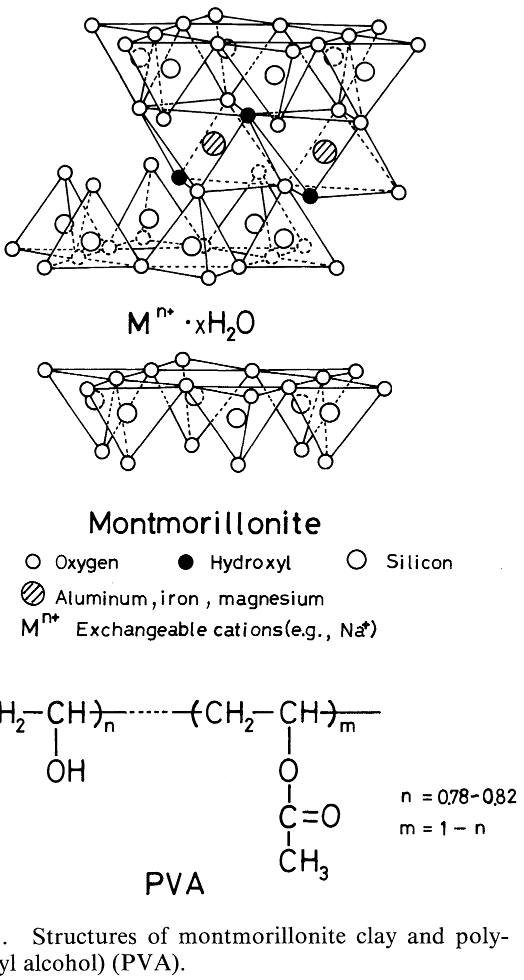

Fig. 1. Structures of montmorillonite clay and poly(vinyl alcohol) (PVA).

structures of the montmorillonite and PVA employed are shown in Fig. 1. Na_2SO_4 solutions of 0.01—1.0 M (1 M=1 mol dm^{-3}) were made up with doubly distilled water. The clay/PVA solution containing 0.5 wt% clay and 0.2 wt% PVA was prepared by mixing the colloidal clay aqueous suspension with PVA.[12]

Apparatus and Procedures. The clay/PVA composite film-coated quartz crystal oscillators were prepared as follows. The both sides of quartz crystal were coated with chromium and gold layers of about 2 and 300 nm thick by vacuum deposition. About 2.0 μl of the clay/PVA aqueous suspension were microsyringed on one side of the quartz crystal oscillator, followed by air-drying and a vacuum drying oven at room temperature for 30 min to complete the solvent evaporation. The thickness of the clay/PVA composite film was about 0.2 μm in the wet state.[12]

The piezoelectric admittance of the oscillators with and without the clay/PVA composite film coating was measured at 25±1 °C in air dried over silica gel, in an atmosphere of moisture (i.e., under the saturated vapor pressure of water at 25 °C) and in contact with Na_2SO_4 aqueous solutions (0.01—1.0 M). In this case, a Yokogawa Hewlett-Packard 4192A-LF impedance analyzer was operated at an internal frequency synthesizer voltage of +0.1 V in a certain frequency range around the resonant frequency of each oscillator. Further details concerning the admittance measurements and the evaluation of the electrical equivalent circuit parameters from the piezoelectric admittance data have been described in our previous papers.[1,16]

Results and Discussion

Conductance Spectra of Montmorillonite/PVA Composite Film-Coated Quartz Crystal Oscillators in Dry Air and Moisture. Figure 2 shows the typical plots of the real part of the piezoelectric admittance against frequency, which we may call as piezoelectric conductance spectra, obtained for the quartz crystal oscillators with and without the clay/PVA film coating in dry air and moisture. When the oscillator was coated with the clay/PVA composite film, the resonant frequency giving the maximum value of conductance shifted to the lower frequency (cf. Spectra A and B). In moisture, the resonant frequency further decreased (Spectrum C). When the oscillator was placed in the dry air again, the resonant frequency (Spectrum D) returned to almost the same value as that for the spectrum B. The quantitative data for these conductance spectra are summarized in Table 1. Based on Fig. 2 and Table 1 the characteristics of the conductance spectra, i.e., the maximum value of the conductance spectrum G_{max} (or the resistance component R) and the full width at half height Δf_{whh} can be regarded to be almost the same for the oscillator with and without the clay/PVA film coating in contact with moisture. The values of Δf_{whh} are almost the same when the oscillator is bare or coated with the clay/PVA film in air and moisture, indicating that the film is rigid. The loading of the film does not cause any additional broadening of the conductance spectrum.[12,19] If the rigidity of the

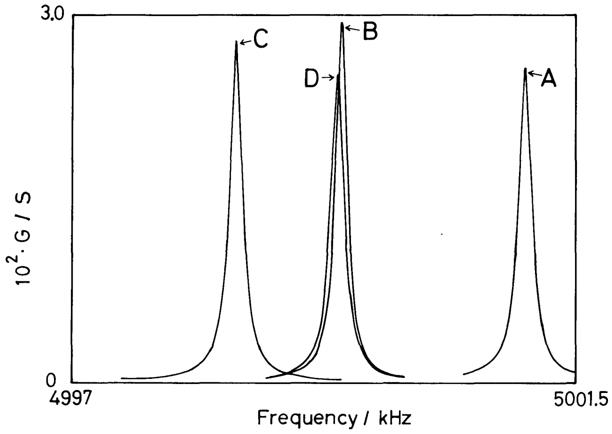

Fig. 2. Conductance spectra of the quartz crystal oscillators without (A) and with (B—D) clay/PVA composite film coating in contact with (A, B, D) dry air and (C) moisture. The measurements were conducted in the order of A, B, C, and D using the same film-coated oscillator.

Table 1. Conductance Spectral Data for Quartz Crystal Oscillators with and without Montmorillonite/PVA Composite Film Coating in Contact with Air or Moisture at 25 °C

System[a]	$10^2 \times G_{max}$[b]	R[c]	Δf_{whh}[d]	f_s[e]	Δf_s[f]	$10^6 \times \Delta m$[j]
	S	Ω	Hz	Hz	Hz	g cm^{-2}
A	2.6	38	144	5001058		
B	2.9	34	138	4999398	−1660[g]	+29.2[k]
C	2.8	36	138	4998458	−940[h]	+16.5[l]
D	2.5	40	141	4999364	+906[i]	−15.9[m]

a) Quartz crystal oscillator without the clay/PVA film coating in air (System A), quartz crystal oscillators with the clay/PVA film coating in air (Systems B and D) and under the saturated vapor pressure of water at 25 °C (System C). The measurements were conducted in the order: A→B→C→D. The amount of the clay/PVA coating: 2.0 μl of the clay/PVA suspension solution (see Experimental section). b) Maximum value of conductance spectrum (conductance at resonant frequency). c) $R=1/G_{max}$. d) Full width at half height of conductance spectra. e) Resonant frequency. f) Difference between resonant frequencies. g) f_s (System B)$-f_s$ (System A). h) f_s (System C)$-f_s$ (System B). i) f_s (System D)$-f_s$ (System C). j) Mass change estimated according to the Sauerbrey equation (Eq. 1). k)—m) Mass changes of k), l), and m) correspond to Δf_s of g), h), and i), respectively.

coating film on the oscillator is less than those of the quartz crystal itself and the gold film deposited onto its faces, the viscoelastic film would prevent the oscillator from vibrating, so that the conductance spectrum would become broader and lower.[18,19)]

Further, we can see that coating the clay/PVA film on the oscillator causes the shift of the resonant frequency to the lower value and that the resonant frequency decreases by exposing the film-coated oscillator to moisture, while it returns to almost the original value when the oscillator is put back into an atmosphere of dry air (see Δf_s values in Table 1). From the values of the resonant frequency change, the mass change can be estimated according to the Sauerbrey equation representing the relationship between frequency and mass:[20)]

$$\Delta m = -C_m \Delta f_s \tag{1}$$

where Δf_s (in Hz) is the frequency change caused by the mass change per unit electrode area of the quartz crystal Δm (in g cm^{-2}) and C_m is a constant which depends on the mechanical properties of the crystal and its fundamental resonant frequency. In the present case, a 5 MHz crystal was used, and so $C_m = 1.76 \times 10^{-8}$ g cm^{-2} Hz^{-1}.[20,21)] From the fact that the values of Δf_{whh} are almost constant for the systems in Table 1 and the discussion above, we may consider the shift in the resonant frequency is due to the mass change. Then, Eq. 1 is applicable and the values of M_{film} and M_{H_2O}, corresponding to the clay/PVA film coating in air and the absorbed (and/or adsorbed) water by the film, were calculated to be 29.2×10^{-6} g cm^{-2} and 16.2×10^{-6} g cm^{-2}, respectively. The latter is the average value for Systems C and D. The values of M_{film} and M_{H_2O} for the clay and the PVA films were also evaluated in a similar manner as above.

Table 2 summarizes the values of M_{film} and M_{H_2O} for the clay, the PVA and the clay/PVA films. The ratio M_{H_2O}/M_{film} represents the capacity for each dry film to absorb and/or adsorb water. The value of M_{H_2O}/M_{film} for the PVA film is the largest in the films examined here, as can be expected from the fact that PVA is a highly hydrophilic polymer and it is well swollen in aqueous media. The value for the clay film is less than half that for the PVA film. The swelling of a clay mineral film in aqueous media is also well realized.[2-8)] For example, in the case of the sodium montmorillonite it has been reported that the basal spacing is increasing from 13.6 to 14.7 Å by soaking it in water for 30 min.[6,22)] The M_{H_2O}/M_{film} value for the clay/PVA film is betweeen those for the clay and PVA film and is close to the latter. This is consistent with the observation in the previous study,[1,10,12)] that the clay/PVA (5:2) composite film[12)] was much more swollen than the clay film was.

Admittance Measurements of Montmorillonite/PVA Composite Film-Coated Oscillators in Contact with Na_2SO_4 Aqueous Media. Figure 3 shows the typical conductance and susceptance spectra, which are the plots of the real and imaginary parts of the piezoelectric admittance as a function of frequency, obtained for the oscillators with and without the clay/PVA film coating in contact with Na_2SO_4 aqueous media of different concentration. For the oscillator without the coating, the damping of the spectrum and the decrease in resonant frequency occurred with increasing the concentration of Na_2SO_4. The behavior is in agreement with that observed recently by Beck et al.[23)] for the naked oscillator in contact with LiCl aqueous solutions. These results could be interpreted on the basis of the relation between the resonant frequency change and the density (ρ) and viscosity (η) of the solution. This correlation has been theoretically derived by Kanazawa and Gordon,[24)] and Bruckenstein and Shay.[25)]

On the other hand, for the clay/PVA film-coated oscillator, the dependence of the conductance and susceptance upon the Na_2SO_4 concentration is largely different from that for the naked oscillator. As seen from Fig. 3B, decreasing electrolyte concentration results in the lowering and broadening of the resonance curves. A similar electrolyte concentration dependence of the conductance and susceptance spectra has been recently found for the oscillator with the clay coating alone.[1)] The results obtained have been explained on the basis of the electrolyte concentration dependence of the electrical equivalent circuit parameters, resistance R, inductance L, and capacitance C. These parameters could be evaluated from the conductance and susceptance spectral data by use of the electrical equivalent circuit model conventionally proposed for a piezoelectric quartz

Table 2. Absorption (and/or Adsorption) of Water by Montmorillonite Film, PVA Film and Montmorillonite/PVA Composite Film at 25 °C

System	M_{film}/g cm^{-2} [d)]	M_{H_2O}/g cm^{-2} [e)]	M_{H_2O}/M_{film} [f)]
Montmorillonite film[a)]	5.17×10^{-5}	1.51×10^{-5}	0.29
PVA film[b)]	1.04×10^{-5}	6.55×10^{-6}	0.63
Montmorillonite/PVA composite film[c)]	2.95×10^{-5}	1.65×10^{-5}	0.56

a) 3.6 µl of 0.5 wt% montmorillonite solution. b) 2.0 µl of 0.2 wt% PVA solution. c) 2.0 µl of montmorillonite (0.5 wt%)/PVA (0.2 wt%) solution. d) According to Eq. 1, the amount (M_{film}) of film coating (in the dry state) was estimated from the difference in resonant frequencies for the oscillators without and with clay, PVA or clay/PVA coating. e) The amount of water absorbed and/or adsorbed (M_{water}) was estimated from the difference in the resonant frequencies in air and under the saturated vapor pressure of water at 25 °C in each system. f) Ratio of M_{H_2O} to M_{film}.

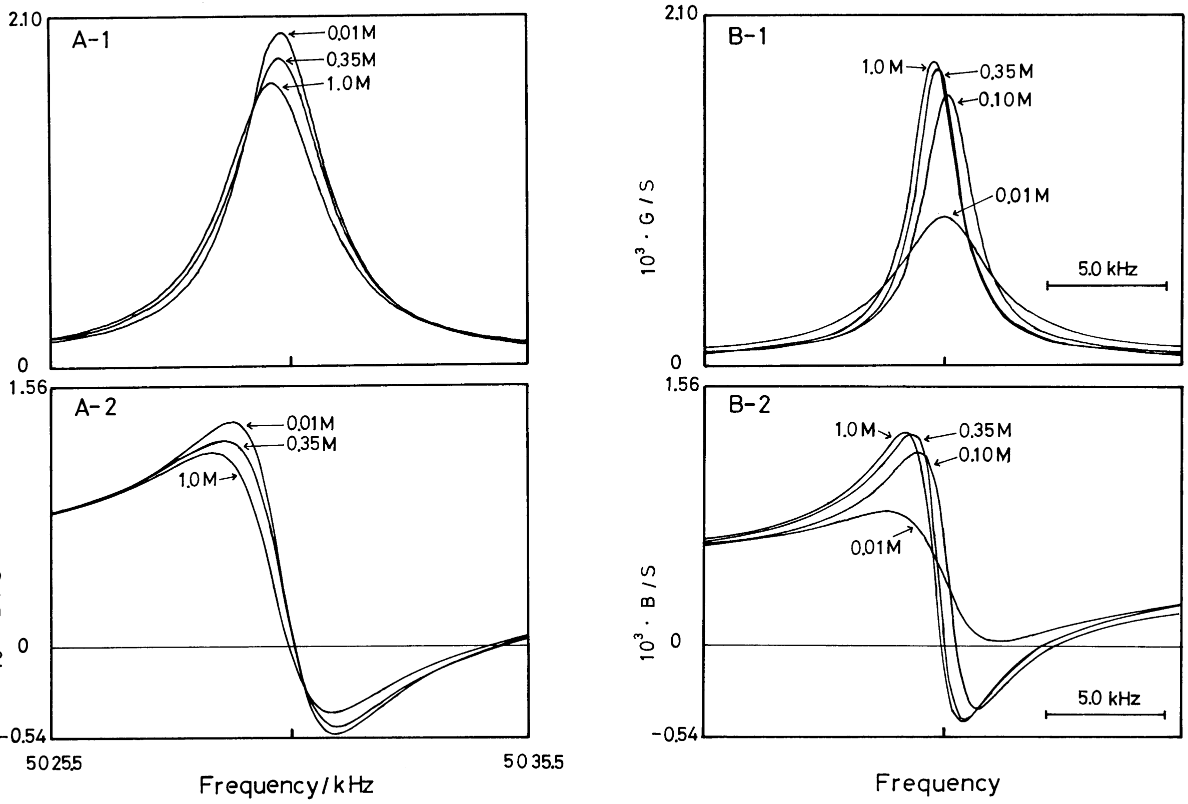

Fig. 3. (A-1, B-1) Conductance and (A-2, B-2) susceptance spectra obtained for (A) naked and (B) clay/PVA composite film-coated oscillators in contact with 0.01—1.0 M Na_2SO_4 aqueous solutions. The starting points on the abscissa axis (representing frequency) in B-1 and B-2 are 4970.7, 4971.0, 4974.0, and 4987.0 kHz for the cases of Na_2SO_4 concentrations of 0.01, 0.10, 0.35, and 1.0 M, respectively.

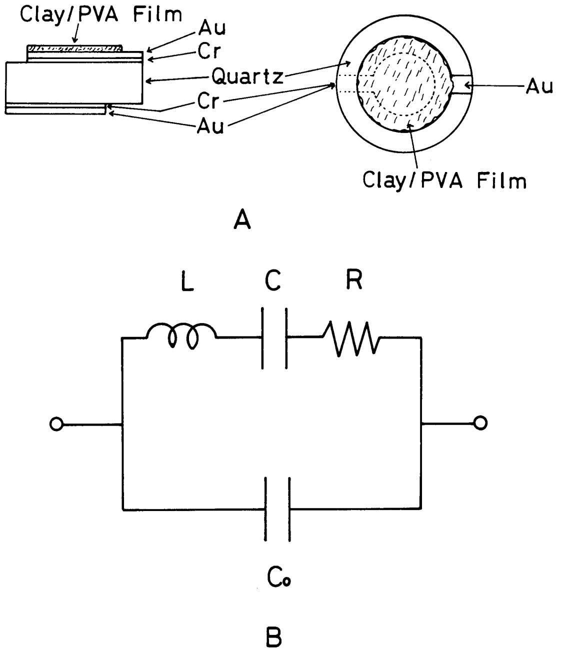

Fig. 4. (A) Schematic top and edge views of a clay/PVA film-coated quartz crystal oscillator. (B) Electrical equivalent circuit for a piezoelectric quartz crystal oscillator. *R*: resistance, *L*: inductance, *C*: capacitance, C_0: capacitance between two parallel-plate metal electrodes on quartz surfaces.

crystal (see Fig. 4).[21,26,27] In the present case, the circuit parameters have also been evaluated from the conductance and susceptance spectra such as those shown in Fig. 3. The results are represented in Fig. 5 as the Na_2SO_4 concentration dependence of these parameters. *R* was almost constant above ca. 0.35 M and increased with decreasing the concentration in the lower concentrations, while *L* and *C* were almost independent of the concentration. According to the principle of electro-mechano-acoustical analogy,[19,26] one can assign the circuit parameters, *R*, *L*, and *C* of a mechanically vibrating oscillator to coefficient of friction, mass and compliance, respectively. Since *L* and *C* are not sensitive to the change in electrolyte concentration, we will confine our discussion to *R*.

Correlation between Electrolyte Concentration Dependence of *R* and Structural Change of Film Matrices. It is interesting to compare between the concentration dependence of *R* for the naked, clay film-coated and clay/PVA film-coated oscillators. The significantly difference was observed, as shown in Fig. 5. The motional resistance *R* represents the dissipation of mechanical energy in the oscillator.[21,26]

For the naked oscillator, *R* slightly increased with increasing the electrolyte concentration. This is ascribable to the increased viscosity (η) and density (ρ) of

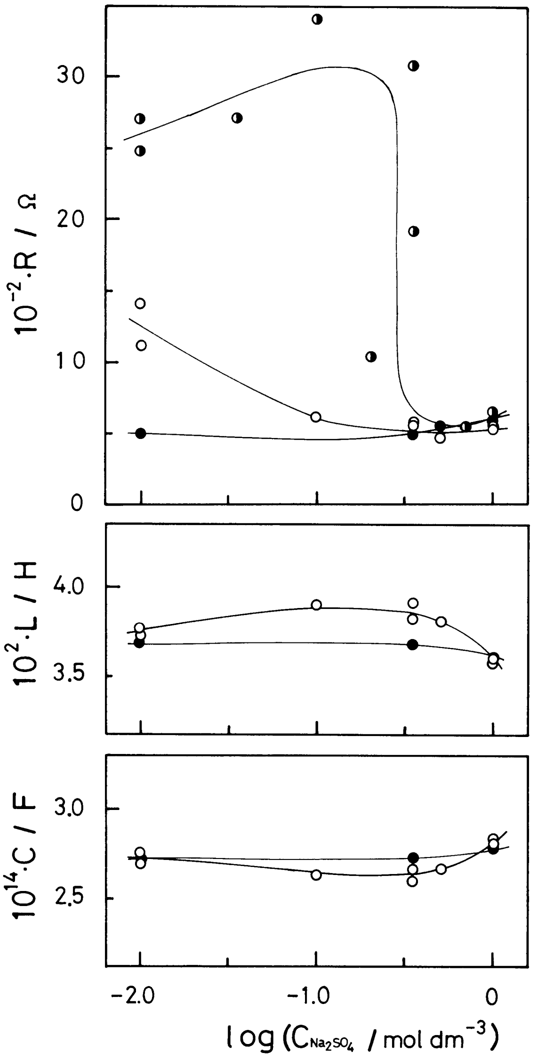

Fig. 5. Concentration dependences of R, L, and C parameters for naked (●) and clay/PVA film-coated (○) oscillators in contact with Na_2SO_4 aqueous solutions. The data for the clay film-coated oscillator, indicated by half-solid circle (◑), are depicted for comparison (Ref. 1).

the solution in contact with the surface of the oscillator, as previously explained on the basis of the idea proposed for the relation between R and ρ and η of the solution:[28)]

$$R = (2\pi f_s \rho\eta)^{1/2} A/k^2 \tag{2}$$

in which f_s is the crystal resonant frequency, A is the crystal electrode area and k is the coefficient of electromechanical coupling of the crystal.

The dependence of R on the electrolyte concentration observed for the clay film-coated oscillator (see Fig. 5) has been understood on the basis of the electrolyte concentration-dependent structural change of the clay film due to the solvent swelling.[1)] It has been experimentally[2—8,9)] and theoretically[29,30)] known that the structure of a clay film changes with an electrolyte concentration. In higher concentrations, the clay film has a face-to-face structure and is relatively rigid, whereas in lower concentrations it posesses an edge-to-face structure and is relatively flexible, swollen and viscoelastic. This behavior could be explained on the basis of the Derjaguin–Landau–Verwey–Overbeek theory proposed for the interaction forces between colloidal particles because the clay film can be regarded as an assembly of colloidal particles. Thus, in the lower electrolyte concentration, it is speculated that the whole clay film on the oscillator dose not necessarily oscillate together with the oscillator itself in such a way as expected for a perfectly elastic thin film coated on the oscillator,[21,25)] so that a perfect match of the acoustic impedance between the clay film coating and the oscillator is not to be achieved. Such a viscous clay film acts as a resistance to the oscillation, resulting in the larger values of R in lower electrolyte concentrations.[24,25,28)] It is concluded that the electrolyte concentration dependence of R obtained for the clay film-coated oscillator system originates from the viscoelastic change of the clay film coated on the oscillator with the electrolyte concentration, and that the structural change of the clay film occurs drastically in a certain range of the concentration (ca. 0.2—0.3 M).

Next, we shall consider the results obtained with the clay/PVA film-coated oscillator. According to the work by Ege et al.[6)] and Greenland,[31)] PVA in the clay/PVA composite film matrix is strongly adsorbed on the external and interlamellar surfaces of the clay platelets. In this case, the adsorption of PVA by the clay is most likely due to the formation of hydrogen bonds between the hydroxyl groups of PVA and the oxygens of the silicate surface of the clay platelets, in addition to the weak interaction between the surface and the hydrocarbon chain of PVA.[6,31)] Consequently, the motional freedom of the individual clay platelets is limited by PVA although the composite film may contain both face-to-face and edge-to-face, cross-linking structures, namely the orientation of the clay platelets is random before exposure to an electrolyte solution. Therefore, in this case, such a drastic structural change with the electrolyte concentration, as observed for the above-mentioned clay film-coated oscillator,[1)] would not be expected to occur or the degree would be small if any. The concentration dependence of R observed for the clay/PVA film-coated oscillator system is qualitatively interpreted from these considerations. The viscoelasticity of the clay/PVA composite film can be considered to change with the concentration of the contacting solution as suggested for the case of the clay film-coated oscillators.[1)] Of course, the degree is much smaller than that in the latter case. In other words, the clay/PVA composite film may be more rigid because of reflecting some additional effects resulting from the introduction of PVA into the clay matrix as mentioned above.

It is obvious from Fig. 5 that above ca. 0.35 M the

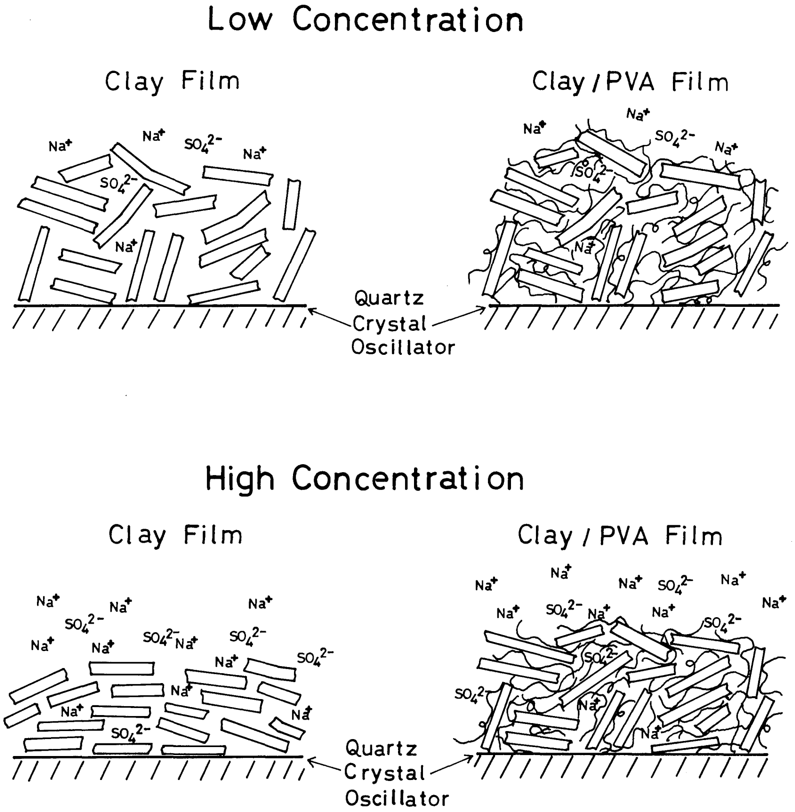

Fig. 6. Schematic illustration of proposed microstructures for clay film matrix and clay/PVA composite film matrix coated on quartz crystal oscillators in contact with Na_2SO_4 aqueous solutions of low (e.g., 0.01 M) and high (e.g., 1.0 M) concentrations. " ▭ " and " ∿ " indicate a clay platelet and PVA, respectively. Solvent (H_2O molecule) is omitted in the illustration.

values of R for the clay film- and clay/PVA composite film-coated oscillators are almost equal to those for the naked oscillator and the concentration dependence of R is common to these three oscillator systems. This suggests that in such a limited range of the electrolyte concentration both the clay film and the clay/PVA composite film may behave rigidly in such a way as expected for a perfectly rigid, elastic thin film coated on the oscillator.[21,26]

On the basis of the results obtained here and the previous studies concerning the structures of the clay and clay/PVA matrices,[2–8,31] the plausible microstructures of these matrices on quartz crystal oscillators in contact with Na_2SO_4 aqueous solutions may be proposed as those illustrated schematically in Fig. 6. The typical microstructures at low and high concentrations (e.g., 0.01 and 1.0 M) are represented. The average distance between the clay platelets is much larger at low concentration than at high concentration for the clay film. For the clay/PVA composite film, on the other hand, though the average distance is of course larger at the low concentration than at the high concentration, the degree is not so significant compared with the clay film. Consequently, it is noted that an introduction of PVA to the clay matrix results in a more rigid structure than in the clay alone,[1] and the from a viewpoint of swelling the clay/PVA composite film is more insensitive to the change in concentration in comparison with the clay film.

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