

Competitive Sorption of Water Vapor and CO₂ in Photocrosslinked PVCA Film for a Capacitive-Type Humidity Sensor

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ABSTRACT: The sorption behavior of water vapor and CO₂ gas in photocrosslinked poly(vinyl cinnamate) (PVCA) film was examined at 30°C under atmospheric pressure. Both the water sorption isotherm and the CO₂ sorption isotherm obtained with quartz crystal microbalance (QCM) method obeyed the simple Langmuir's equation. Water vapor/CO₂ mixed-gas sorption isotherms were also obtained. Total amount of sorbed mixed gases was clearly influenced by the partial pressure of water vapor (p_w) and CO₂ gas (p_c) in the atmosphere. A modified Langmuir's equation based on a dual-site model was employed for predicting the competitive adsorption isotherm, and the isotherm was clearly described by the equation. The theoretically estimated amount of adsorbed water at the constant p_w decreased slightly with increasing p_c . The effect of this phenomenon on the sensitivity of the capacitive-type relative humidity sensor was examined. As expected, the electrical capacitance of the sensor at the constant relative humidity decreased because of the coexistence of CO₂ gas. However, the influence was quite small in the CO₂ concentration range in the ordinary environment. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 401–407, 2002

Key words: competitive sorption; dual-site model; photocrosslinked PVCA; humidity sensor

INTRODUCTION

It is interesting to investigate the theoretical and practical significance of gas sorption behavior in various crosslinked glassy polymers. From a theoretical point of view, sorption of gases in a crosslinked polymer exhibits various unexpected behaviors because of the rigid structure of such polymers.^{1–5} The restricted motions of polymer chain segments allows for much more sensitive size and shape discrimination. However, very few investigations of sorption in crosslinked polymers

have been performed. From a practical point of view, preliminary work in our laboratory has shown that crosslinked polymers, which have a carbonyl group as a weak hydrophilic site, are suitable for a capacitive-type relative humidity (RH; relative water vapor pressure) sensor.^{1–3,6,7} Highly photocrosslinked poly(vinyl cinnamate) (PVCA) is one of several excellent materials that satisfy the above requirements. In addition, sorption behavior of various gases in photocrosslinked PVCA was examined to investigate the selectivity of the sensor.^{2,3} In a series of studies, it was found that photocrosslinked PVCA film sorbed CO₂ gas.^{4,5} Humidity sensors are used in air and air necessarily contains CO₂. This means that there is the possibility that the coexisting CO₂ gas could influence the humidity sensor output.

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In this study, the competitive sorption behavior of water vapor and CO₂ gases in photocrosslinked PVCA film is discussed. The results were analyzed by an extension of Langmuir's theory of adsorption, which is based on the so-called dual-site model (a CO₂-accessible site and a CO₂-inaccessible site, respectively) reported previously.⁸ Furthermore, a capacitive-type RH sensor was prepared by using photocrosslinked PVCA film. The effect of coexisting CO₂ on the humidity sensitivity of the prepared sensor was examined.

EXPERIMENTAL

Materials and Devices

PVCA was purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI) and used without further purification. PVCA undergoes an intermolecular photodimerization of the cinnamate moiety in the solid state, resulting in a glassy crosslinked film. For the sorption measurement, the PVCA solution in toluene was spin-coated and photocrosslinked on an AT-cut (temperature compensated) quartz crystal oscillating element (4 MHz). The thickness of the film was ca. 5 μm. The degree of crosslinking was determined by using FTIR analysis, and the fresh film having ca. 85% degree of crosslinking was used for each measurement. A capacitive-type humidity sensor with a parallel plate capacitor structure was also prepared. Details of the procedures by which these devices were prepared were described elsewhere.^{2,5}

Experimental

The devices were placed in a small thermostated measuring chamber. The amount of sorbed gases was measured gravimetrically by quartz crystal microbalance (QCM) method. The oscillation frequency of the quartz crystal was monitored with a frequency counter. Electrical capacitance was measured at 100 kHz by using an LCR meter. These measurements were performed in flows of CO₂ and N₂ at various partial pressures of water vapor under atmospheric pressure. The partial pressure of CO₂ in the measuring atmosphere was varied by mixing high-purity CO₂ and N₂ gases supplied from each gas cylinder. The partial pressure of the water vapor was varied by controlling the mixing ratio of a dry N₂ gas and a water-saturated N₂ gas, which was prepared by

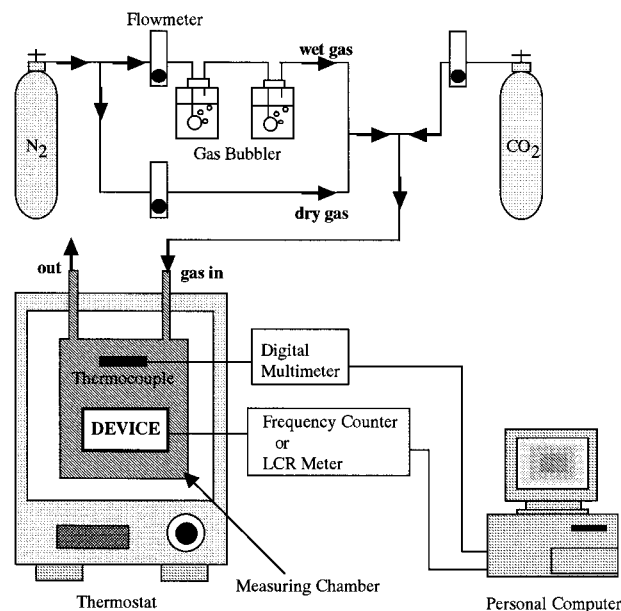


Figure 1 Gas flow system used to provide flows of CO₂ and N₂ at various water vapor pressures and its experimental setup.

bubbling the N₂ gas through water. The experimental setup is shown in Figure 1.

RESULTS AND DISCUSSION

Sorption of Water Vapor

The water sorption ability of photocrosslinked PVCA film and uncrosslinked one was measured as a function of the partial pressure of water vapor (p_w). The sorption isotherms obtained at 30°C are shown in Figure 2. The amount of sorbed water, W_w , which was defined as milligrams of water sorbed in 1 g of dry polymer, was plotted on the ordinate. It is observed that there is a distinction between the photocrosslinked PVCA film and that of the uncrosslinked one. The isotherm for the uncrosslinked PVCA is almost linearly predicted by Henry's law. On the other hand, the isotherm for the photocrosslinked PVCA is concave toward the abscissa. In addition, the water sorption ability is enhanced by crosslinking the film. The water molecule is highly condensable because of its highly polar and amphiprotic structure. If the clustering of water molecules occurs in the film, the sorption increases abruptly at high pressures. However, this is not the case for the sorption behavior of the photocrosslinked PVCA, as observed in Figure 2.

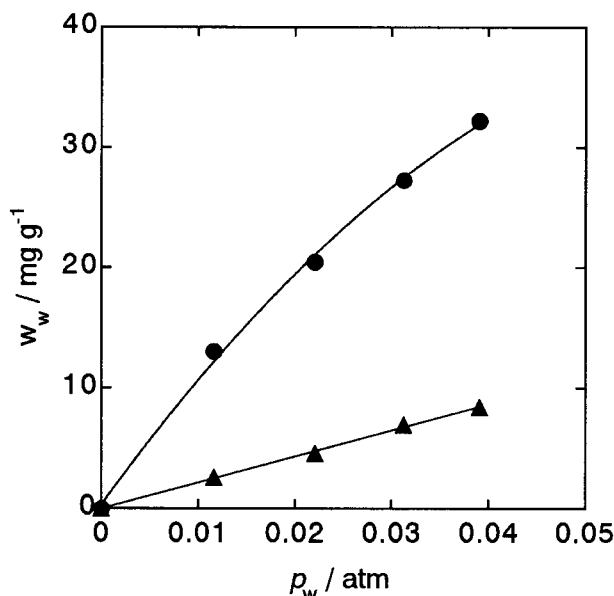


Figure 2 Water sorption isotherm of PVCA film obtained at 30°C under atmospheric pressure: (●) photocrosslinked and (▲) uncrosslinked.

It is well known that sorption of gases in a glassy polymer is accurately described by the dual-mode sorption model.⁹⁻¹³ Sorption of water vapor is not an exception. Shigetomi et al. reported that the dual-mode sorption model is also effective for analyzing the isotherms of water vapor sorption in a glassy PET film.¹⁴ In the case of crosslinked glassy polymers, we have pointed out in an earlier article that the water sorption in the highly crosslinked polyimide film obeyed the simple Langmuir's rule.⁸ This is because the crosslinking structure depresses the segment motion of the main chain more than that of a glassy polymer and results in a small contribution of Henry-type sorption (dissolution in the polymer) to the total sorption. In such a case, the microvoids in the polymer seem to play a dominant role in the sorption. The increase in sorption ability correlates with the increase in the number of microvoids that occurred as a result of the crosslinking reaction. In fact, the isotherm of the photocrosslinked PVCA film is adequately approximated by a simple Langmuir-type equation for unimolecular adsorption, as follows¹⁵:

$$W_w = W_w^s (K_w p_w / (1 + K_w p_w)) \quad (1)$$

where W_w^s is a saturation constant and K_w is a constant at a given temperature. A linear rela-

tionship between $1/W_w$ and $(1/p_w)$ was confirmed for the present isotherm, and the obtained W_w^s value was 75.5 mg/g polymer and K_w was 17.9 atm⁻¹.

Sorption of CO₂

Sorption behavior of CO₂ in the photocrosslinked PVCA film and the uncrosslinked PVCA film have been reported previously.^{4,5} The amount of sorbed CO₂ obtained in a dry atmosphere under atmospheric pressure, W_c , is plotted as a function of the partial pressure of CO₂ (p_c) in Figure 3. Both isotherms are concave toward the abscissa. The CO₂ sorption ability is also enhanced by crosslinking the film. The sorption of CO₂ in a glassy polymer is usually described by the dual-mode sorption model, especially at a high CO₂ pressure.^{16,17} However, a good linear relationship between W_c and $1/p_c$ (a Langmuir-type isotherm) was obtained for the present photocrosslinked PVCA.⁵ The results also suggest that microvoids in the crosslinked polymer act as an important adsorption site. The calculated Langmuir's saturation constant (W_c^s) was 11.9 mg/g polymer and K_c was 1.07 atm⁻¹.

Adsorption Model for Water Vapor and CO₂ Molecules

The obtained isotherms for water vapor and CO₂ in the photocrosslinked PVCA film suggest that

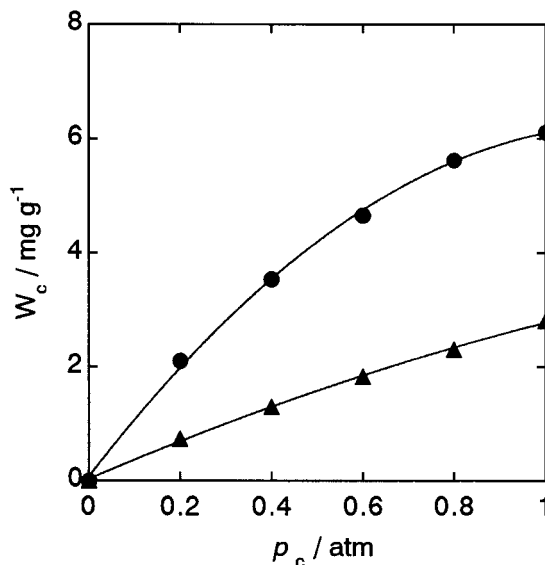


Figure 3 CO₂ sorption isotherm of PVCA film obtained at 30°C under atmospheric pressure: (●) photocrosslinked and (▲) uncrosslinked.

the sorption of these gases is adequately approximated by the simple adsorption on the surface of the microvoids. However, the CO_2 adsorption ability was considerably small than that of water. The above Langmuir's saturation constants, W_w^s and W_c^s , were converted into moles of solutes, yielding 4.2×10^{-3} mol water/g (M_w^s) and 2.7×10^{-4} mol CO_2 /g (M_c^s), respectively. The ratio α ($=M_c^s/M_w^s$) is equal to 6.4×10^{-2} . The adsorption site of CO_2 is believed to be the carbonyl group that appears on the surface of the microvoids and is the same as that of the H_2O molecule. The difference between M_w^s and M_c^s can be attributed to a variety of many factors. However, the most important factor is the morphology of the crosslinked glassy polymer. The distribution of microvoids of various sizes is expected in a highly crosslinked film. Further, these microvoids are linked three dimensionally in the bulk of the film, and the surface of the microvoids is complex in shape. The difference in molecular size of H_2O and CO_2 may affect the adsorption behavior in such complex microvoids. As described elsewhere, one half the molar volume of CO_2 is estimated for H_2O from the van der Waals volume ($10.3 \text{ cm}^3/\text{mol}$ for H_2O and 19.7 for CO_2) in a glassy polymer.⁸ These factors lead to the idea of a dual-site model (Fig. 4) (i.e., a CO_2 -accessible site and CO_2 -inaccessible site). It should be noted here that this figure is given in a simplified form for a clear understanding of the model. Microvoids smaller than an H_2O molecule were omitted, because both gases cannot be adsorbed in such microvoids. Water molecules can enter both the smaller microvoids (A) and the larger microvoids (B) [Fig. 4(a)]. However, CO_2 molecules enter only the microvoids (B) which are larger in size than the CO_2 molecules [Fig. 4(b)]. Moreover, a single CO_2 molecule requires a larger surface area for adsorption and may occupy plural sites for the H_2O molecule in the complex microvoids. These phenomena seem to result in the difference in the sorption ability for H_2O and CO_2 . Consequently, in the case of competitive adsorption [Fig. 4(c)], the above two factors should be considered in the adsorption analysis.

With the help of a few simplifying assumptions, it is possible to deal with an isotherm derivation for competitive adsorption. An extension of Langmuir's theory of adsorption to the case of gas mixtures leads to the following equation. On the basis of the dual-site model, three assumptions were made for competitive adsorption as follows. First, the number of total adsorption sites

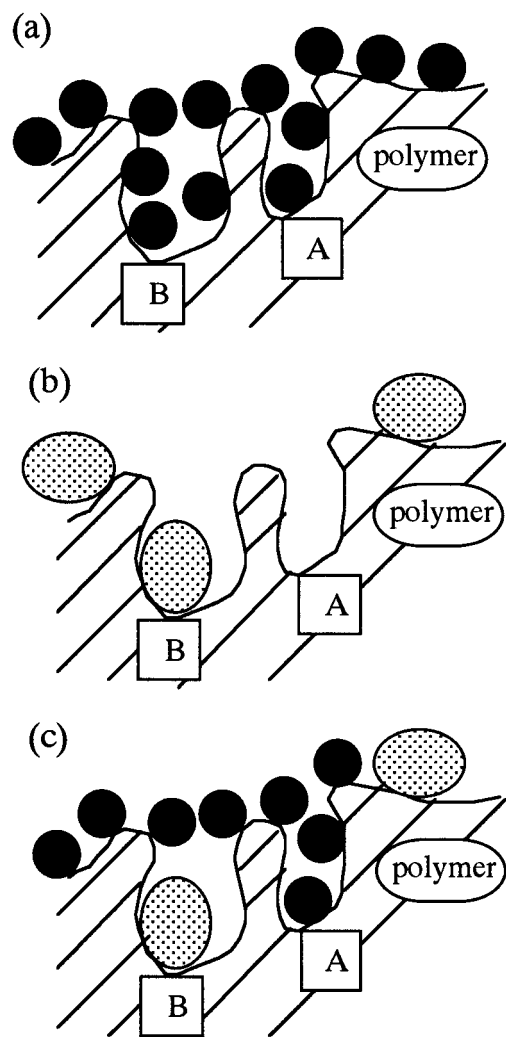


Figure 4 Schematic presentation of adsorption of H_2O and CO_2 molecules in the microvoids: (a) adsorption of H_2O molecules, (b) adsorption of CO_2 molecules, and (c) competitive adsorption of H_2O and CO_2 molecules.

is equal to M_w^s . Second, n adsorption sites are consumed for adsorption of one CO_2 molecule. Third, only a site B in the microvoids (B) is effective for CO_2 adsorption (competitive adsorption occurs only on the site B). In this case, the fraction of the site B in relation to the total site is equal to $n\alpha$ ($\alpha = M_c^s/M_w^s$). In other words, under the conditions of competitive adsorption, the number of sites A is equal to $M_w^s - n\alpha M_w^s$ and that of sites B is $n\alpha M_w^s$. The number of sites free from gas is $M_w^s - n\alpha M_w^s - M_w^A$ for site A and $n\alpha M_w^s - M_w^B - nM_c$ for site B, where M_w^A and M_w^B are the number of adsorbed H_2O molecules on site A and site B and M_c is the number of moles of adsorbed

CO₂ on site B at the constant p_w and p_c , respectively. If the adsorption energy of both site A and site B is the same for H₂O, M_w^A and M_w^B will be equal to $(1 - n\alpha)M_w$ and $n\alpha M_w$ ($M_w = M_w^A + M_w^B$), respectively. Therefore, we can obtain the number of total sites free from gas, which is $M_w^s - M_w - nM_c$. The rate of adsorption of H₂O, r_w , is equal to $k_w p_w (M_w^s - M_w - nM_c)$, where k_w is a constant at a given temperature. The rate of desorption, r'_w , can be expressed by the equation $r'_w = k'_w M_w$. At equilibrium, r_w is equal to r'_w and leads to

$$k_w p_w (M_w^s - M_w - nM_c) = k'_w M_w \quad (2)$$

Substitution of K_w for k_w/k'_w gives

$$M_w = K_w p_w (M_w^s - M_w - nM_c) \quad (3)$$

Similarly, the rate of adsorption of CO₂, r_c , is equal to $k_c p_c [(M_w^s - M_w)n\alpha - nM_c]$, because the number of sites B free from gas is $n\alpha M_w^s - n\alpha M_w - nM_c$. The rate of desorption is $r'_c = k'_c nM_c$. At equilibrium, the following equation is obtained:

$$nM_c = K_c p_c [(M_w^s - M_w)n\alpha - nM_c] \quad (4)$$

where $K_c = k_c/k'_c$. From eqs. (3) and (4),

$$M_w = K_w p_w X M_w^s / (1 + K_w p_w X + K_c p_c) \quad (5)$$

and

$$M_c = \alpha K_c p_c M_w^s / (1 + K_w p_w X + K_c p_c) \quad (6)$$

where $X = [1 + (1 - n\alpha)K_c p_c]$. Finally, we can obtain the individual amount of adsorbed gases in the case of competitive adsorption as follows:

$$W_w = M_w \times N_w = N_w K_w p_w X M_w^s / (1 + K_w p_w X + K_c p_c) \quad (7)$$

and

$$W_c = M_c \times N_c = N_c \alpha K_c p_c M_w^s / (1 + K_w p_w X + K_c p_c) \quad (8)$$

where N_w and N_c represent the molecular weight of H₂O and CO₂, respectively. Constants involved in eqs. (7) and (8) were determined for separate gases and were described in the previous sections.

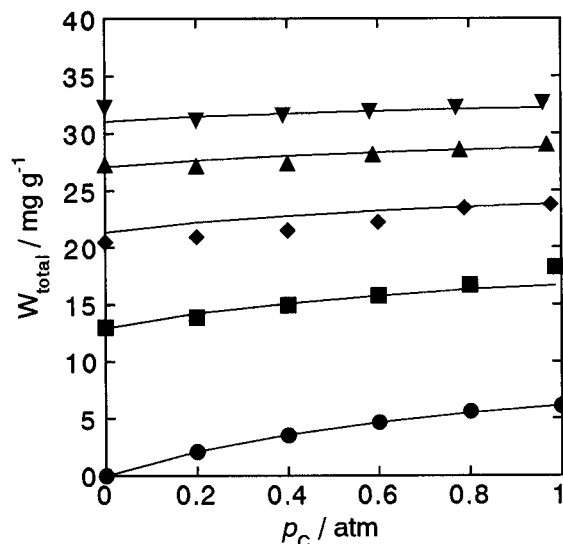


Figure 5 Competitive adsorption isotherm of H₂O and CO₂ in the photocrosslinked PVCA film measured at 30°C under atmospheric pressure: (●) $p_w = 0$, (■) 0.0116, (◆) 0.0221, (▲) 0.0313, and (▼) 0.0391, respectively.

In the case in which each gas occupies the same site equally ($\alpha = 1$), n essentially results in unity.

Competitive Adsorption of H₂O and CO₂ Molecules

The adsorption experiments were performed under the condition of the coexistence of water vapor and CO₂ gas. The result is shown as a function of p_c at different p_w in Figure 5. The ordinate is the experimentally obtained total adsorption amount of the mixed gases, W_{total} . In a low p_w region, W_{total} was clearly affected by p_c because of the small amount of adsorbed water. On the other hand, the variation of W_{total} with p_c decreases in a higher p_w region. Adsorption of H₂O molecules becomes a dominant factor in this region.

From eqs. (7) and (8), individual amounts of adsorbed gases, W_w and W_c , were estimated for various choices of the parameter n . By using these values, the total amount of adsorbed gases ($=W_w + W_c$) was predicted and compared with the experimental results. For example, Figure 6 is a comparison between experimental data and the predicted results at $p_w = 0.0391$ atm. In the case of $n = 3-4$, eqs. (7) and (8) proved to be fairly satisfactory for predicting the competitive adsorption of H₂O and CO₂. The estimated n value is an experimentally obtained mean value based on the present adsorption model, and it is difficult to

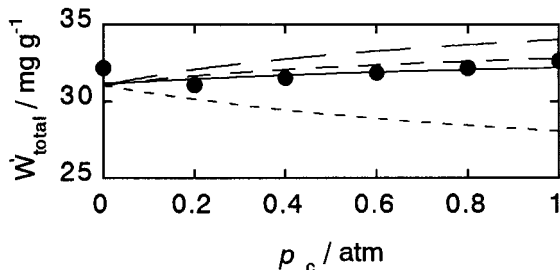


Figure 6 Comparison between experimental data and the predicted results at 30°C and $p_w = 0.0391$. Symbols are the experimental values and lines are the predicted results from eqs. (7) and (8) using (---) $n = 1$, (- · -) $n = 3$, (—) $n = 4$, and (· · ·) $n = 10$.

explain its physical meaning clearly from a microscopic point of view at the present stage. At any rate, it was confirmed that the competitive adsorption behavior on the complex surface was well described theoretically by the present simple treatment.

Effect of Coexisting CO_2 on the Humidity Sensitivity

Predicted W_w and W_c values estimated from eqs. (7) and (8) using $n = 4$ at different p_w are plotted against p_c in Figure 7. It is shown that W_c decreases slightly with increasing p_w at constant p_c

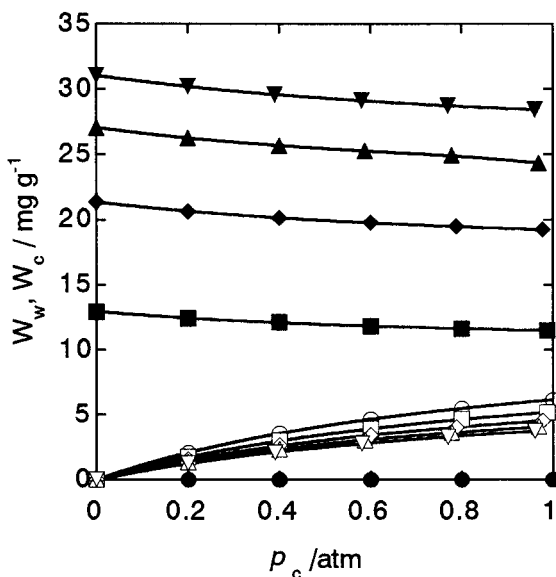


Figure 7 Dependence of W_w and W_c evaluated from eqs. (7) and (8) on p_c at different p_w : symbols are the same as in Figure 5. Closed symbols show W_w ; open symbols show W_c .

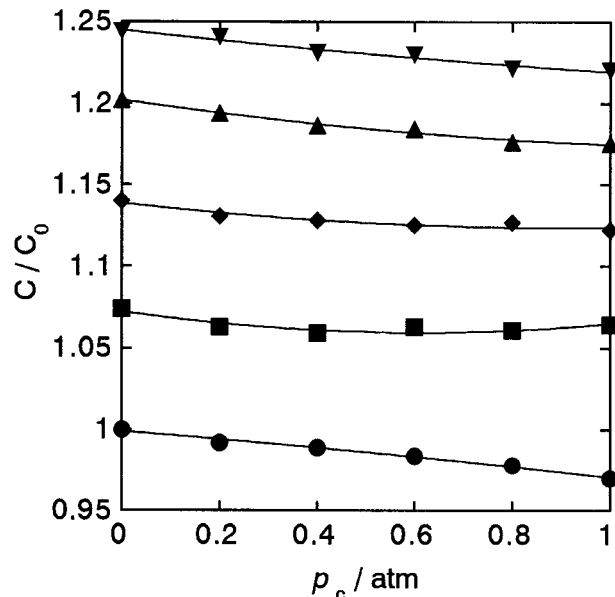


Figure 8 Electrical capacitance change of photocrosslinked PVCA film with relative humidity measured at different p_c at 100 kHz and 30°C: (●) 0% RH ($p_w = 0$), (■) 27.6 (0.0116), (◆) 52.7 (0.0221), (▲) 74.7 (0.0313), and (▼) 93.3 (0.0391), respectively.

as a result of competitive adsorption. W_w also decreases with increasing p_c at constant p_w .

Capacitive-type RH sensors employ a simple sensing mechanism. The water sorption and desorption of the sensing polymer changes its effective permittivity. This phenomenon causes a sensor-capacitance change. Consequently, the electrical capacitance is directly related to the amount of sorbed water in the polymer. Indeed, adsorption of CO_2 does not directly affect the electrical capacitance, because a CO_2 molecule is a nonpolar compound. However, the decrement of W_w as a result of competitive adsorption, as shown in Figure 7, is responsible for the sensor output change. The electrical capacitance of the photocrosslinked PVCA film was measured under the condition of the coexistence of water vapor and CO_2 at 100 kHz and 30°C. Figure 8 shows the ratio of the electrical capacitance measured at $X\%$ RH (C_X) to the electrical capacitance at 0% RH (C_0) as a function of p_c . As expected, the C_X/C_0 value decreased with an increase in the partial pressure of coexistent CO_2 gas. However, it is well known that the concentration of CO_2 is about 0.03% in air. In addition, the fluctuation of the CO_2 concentration seems to be small except for in the case of exhaust gases. Consequently, it can be concluded that the effect of CO_2 on the sensitivity

of the capacitive-type RH sensor using photocrosslinked PVCA is quite small when it is used in an ordinary environment.

CONCLUSION

From the above considerations, several conclusions can be drawn.

The microvoids in the crosslinked glassy polymer play a dominant role in the water vapor and CO₂ gas sorption. This is because the crosslinking structure depresses the segment motion of the main chain and the microvoids in the polymer seem to play a dominant role in the sorption. The modified Langmuir's equation based on the dual-site model predicted the competitive adsorption of H₂O and CO₂ molecules on the surface of the microvoids, which should lower the amount of adsorbed H₂O.

In agreement with the above phenomenon, the sensitivity of the capacitive-type humidity sensor using photocrosslinked PVCA decreased in the presence of coexisting CO₂ gases. However, the effect was quite small in the concentration range in an ordinary environment.

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