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NOTES

Permeability of Double-Layer Films II

TSUNETO KURIYAMA, MICHIHARU NOBUTOKI, and MICHIO NAKANISHI

Abstract ☐ Most of the combinations of coating films showed "two-sided" permeability, while this property has not been reported for films composed of hydrophobic layers only. Any coating film is more or less hydrophilic, and its water vapor permeability varies according to the mean humidity condition in which the film is placed. It was found that double-layer films with "two-sidedness" have characteristic relations (as classified into Groups α, β, γ, and δ) between specificity of permeability and humidity range.

Keyphrases ☐ Permeability, two-sided—double-layer films ☐ Double-layer films—permeability, relationship of water vapor, humidity

In the first part of this study, the authors reported the so-called "two-sided" directional property of the water vapor permeability of double-layer films, and classified this property into four groups: α, β, γ, and δ (1). In double-layer films with two-sided water vapor permeability of the Group α, the permeability is either smaller or greater than that of either component layer, depending on the direction of permeation. The latter feature is a phenomenon that cannot be elucidated in a simple manner. Ninneman and Simerl (2) studied the permeability of multilayer films and introduced the following equation:

$$\Delta p = Q \sum_{i=1}^{n} \frac{l_i}{P_i} \qquad \text{(Eq. 1)}$$

where Δp stands for the difference in water vapor pressure between the higher humidity atmosphere and lower humidity atmosphere (*i.e.*, $p_1 - p_2$), Q is the permeability of an n-layer film, l_i is the thickness of the ith layer in the n-layer film, and P_i is the permeability coefficient of the ith layer. This equation may estimate the permeability of the multilayer film at a certain condition, where the material and the thickness of each component layer are given. It cannot explain the two-sided property of the multilayer film, however, because the permeability thus calculated is independent of the permutation of component layers of a film. In other words, Eq. 1 is practically applicable to the hydrophobic film only but not to the coating film, which is more or less of a hydrophilic nature.

Equation 3 is derived from Eq. 2 (1), which is known to be applicable to the hydrophobic film.

$$q = P \frac{p_1 - p_2}{l} At \qquad \text{(Eq. 2)}$$

$$\frac{1}{Q} = \frac{At}{q} = \frac{l}{P \Delta p} \qquad \text{(Eq. 3)}$$

where A is the area of film through which water vapor is permeated, t is the time of permeation, and q is the quantity of moisture permeated. But Eq. 3 does not always apply to the coating (hydrophilic) film. While $1/Q$ should be proportional to l according to Eq. 3, previously reported experiments (1) revealed that the value of $1/Q$ for $l=0$ did not come to zero in spite of the linearity of the relationship between $1/Q$ and l. This finding suggests that the permeability of the coating film is different from that of the usual hydrophobic film and its behavior is rather complex. The two-sided property of the coating film may be attributed to these very facts.

Takeda (3), studying the permeability of cellulose films, introduced the following equation:

$$\frac{1}{Q} = \frac{l}{P \Delta p} + \frac{2}{k \Delta p} \qquad \text{(Eq. 4)}$$

where k is a coefficient which indicates how easily water molecules drive into the film from the higher humidity atmosphere. This equation explains that the relationship between $1/Q$ and l is not proportional;
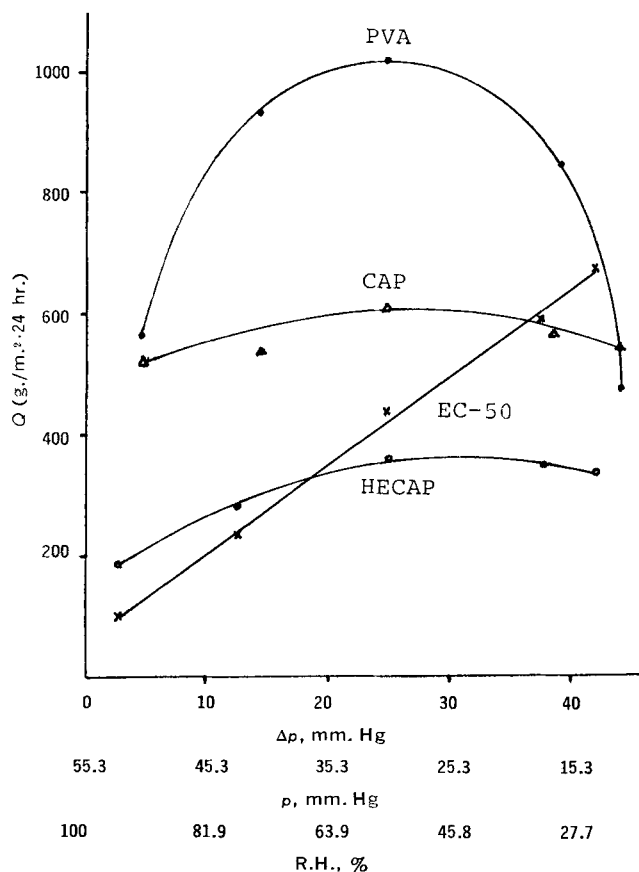
Figure 1—*Relationship between* Q *and* Δp. *Temperature,* $40°$; *thickness of film,* 0.1 *mm.;* $p_1 = 100\%$ $R.H = 55.3$ *mm. Hg; and* $\Delta p = p_1 - p$.

Figure 2—*Relationship between* P *and* Δp. *Temperature,* $40°$; *thickness of film,* 0.1 *mm.;* $p_1 = 100\%$ $R.H. = 55.3$ *mm. Hg; and* $\Delta p = p_1 - p$.

i.e., the value of $1/Q$ is not zero even when the value of l equals zero. The authors attempted to elucidate various features of two-sidedness by using Eq. 4, but the results did not clarify every finding of a series of experiments.

The present report describes the results of a study of the two-sided permeability of double-layer films and the permeability of the component single-layer films according to the changes of p_1 and p_2. The symbol p_1 means a certain fixed water vapor pressure at the higher humidity side, and p_2 means that at the lower humidity side. The symbol p is used as the variable of either p_1 or p_2.

EXPERIMENTAL

Method—Experiments were performed in the same manner as reported in the preceding part of this study (1). Various p_2 (water vapor pressure of lower humidity atmosphere) conditions and temperatures were generated by a Tabai Lucifer model TL-21P. The permeation cell containing a solution to generate various p_1 (water vapor pressure of higher humidity atmosphere) conditions in the cell was placed in the cited apparatus. The weight decrease of the cell after permeation was measured.

Materials—The materials used are the same as in the previous report (1); they are designated by abbreviations defined in that paper.

RESULTS AND DISCUSSION

The permeability (Q) of the single films was determined at $40°$, where water vapor pressure at the higher humidity side p_1 was 55.3
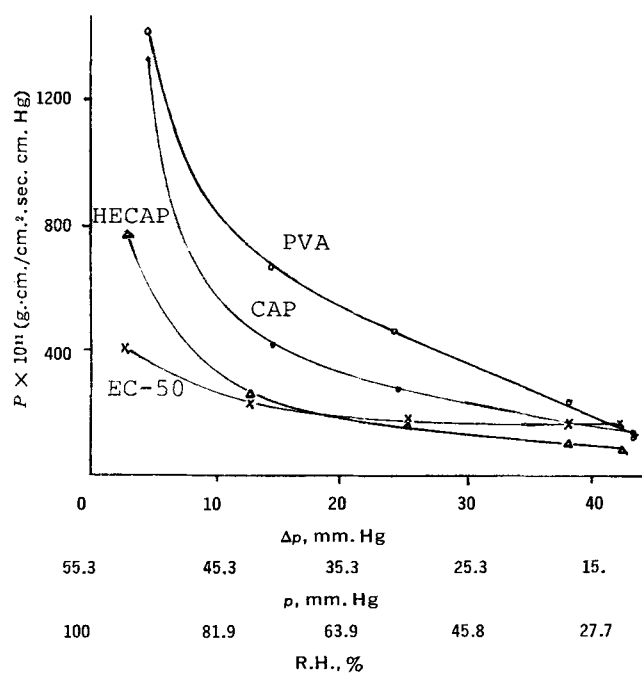
mm. Hg (relative humidity, 100%), and water vapor pressure at the lower humidity side p_2 was varied over a wide range. Some of the results thus obtained are illustrated in Fig. 1.

The figure shows the results with 0.1-mm.-thick films only; similar results were obtained with films of various thicknesses.
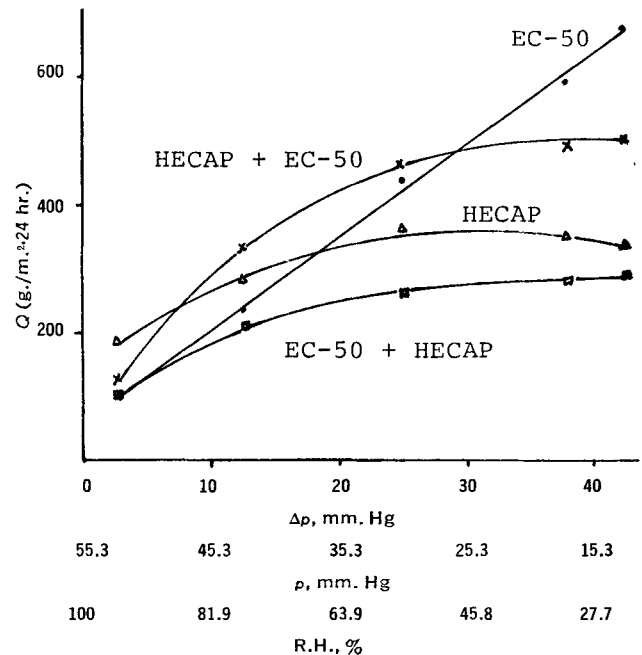

Figure 3—*Relationship between* Q *and* Δp. *Temperature,* $40°$; *composition of double-layer films:*

(*Higher humidity side*)		(*Lower humidity side*)
HECAP	+	*EC-50*
EC-50	+	*HECAP*

Thickness of film: double-layer film, 0.05 *mm.* $+$ 0.05 *mm.; single film,* 0.1 *mm.;* $p_1 = 100\%$ $R.H. = 55.3$ *mm. Hg; and* $\Delta p = p_1 - p$.

Since it was difficult to obtain directly in a single experiment films of exactly 0.1-mm. thickness, several films were selected so that the thickness of each film might be distributed in a range from 0.05 to 0.4 mm. and the respective water vapor permeability was measured at various humidity conditions. Plotting the relationship between permeation resistance $(1/Q)$ and film thickness (l) gave a straight line. Thus, the permeability (Q) of the film of a given thickness (l) in various conditions could be obtained.

Figure 1 suggests some noteworthy points. According to Eq. 2, the relationship between Q $(=q/A)$ and Δp $(=p_1 - p_2)$ should be linear and proportional. As shown in Fig. 1, however, most of the obtained curves do not agree with Eq. 2. In particular, the value of Q for PVA does not increase after the maximum point, even when the value of Δp increases. The cause of this apparently controversial phenomenon may be that the permeability, Q, depends not only on the pressure difference between the higher vapor pressure side and the lower side, but also on the mean humidity condition to which the test film is subjected. This feature may be called the water vapor pressure dependency of permeability.

The permeability coefficient (P) for a hydrophobic film is constant, because water vapor does not interact with the film, and the experimental data correspond to Eq. 1 or 2. On the other hand, for hydrophilic films such as coating films, the value of P changes according to the humidity condition, because water vapor interacts with the film; thus Eq. 1 or 2 does not apply to the hydrophilic film. The relationship between P and Δp was obtained from Eq. 2 by using the data of Fig. 1. Figure 2 shows the results obtained. The value of P changed sharply, especially for the PVA film.

Figure 3 illustrates the relationship between Q and Δp for the double-layer film, which has the remarkable two-sided feature of permeation. For comparison, this figure also shows the curves obtained with each single-component film. The permeability Q of the single films and of the double-layer film is expressed on the basis of 0.1-mm. thickness. It was found (Fig. 3) that two-sided features, classified as Group α and Group δ (1), occurred over different humidity ranges. These features will, of course, change according to the sort of double-layer film or the combination of single films used therein.

SUMMARY

With both single-component films and a double-layer film, the relationship between water vapor permeability (Q) and humidity condition was studied. It was found that the permeability of the films depended not only upon the difference in vapor pressure (Δp) between the higher and lower humidity sides, but also upon the mean humidity condition to which the test film was subjected. It was also found that a double-layer film with two-sided permeability displayed the feature of Group α in a certain humidity range and the feature of Group δ in another humidity range.

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GLC Determination of Guaiacol Glyceryl Ether in Blood

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Abstract □ A method has been developed for the determination of guaiacol glyceryl ether in blood by extraction with methylene chloride followed by conversion to the heptafluorobutyrate ester and quantitation using an electron-capture detector. Blood levels following oral administration of the drug indicate a rapid absorption and elimination with a half-life of 1 hr.

Keyphrases □ Guaiacol glyceryl ether—GLC determination, in blood □ NMR—identification □ GLC—determination, guaiacol glyceryl ether, in blood

Guaiacol glyceryl ether (GGE) has been used for many years as an expectorant and, more recently, it has been claimed to have activity as a muscle relaxant (1) and as an hypocholesteremic (2–5), and to reduce platelet adhesiveness (6). In spite of its extensive use and study, no methods appear to be available for its determination in man following usual dosages. Morgan *et*

al. (7) studied blood levels in dogs, and Mizutani and Naito (8) have determined blood levels in rabbits. However, relatively large doses were administered in each case, and these methods do not appear adaptable to present needs. Therefore, a method has been developed using GLC which appears to be satisfactory.

EXPERIMENTAL

The method is based on extraction of GGE from blood with methylene chloride and conversion to the heptafluorobutyrate ester and quantitation by GLC using an electron-capture detector. Mephenesin [3-(o-toloxy)-1,2-propanediol] is used as an internal standard.

The procedure is carried out as follows. To 5.0 ml. of blood, add 1.0 mcg. of mephenesin, 3 ml. of distilled water, and 0.5 ml. of 2 N H_2SO_4. Then extract with 20 ml. of redistilled methylene chloride by shaking for 10 min. Separate the phases by centrifuging, and dry the methylene chloride extract by passing it through a layer of anhydrous sodium sulfate in a funnel. Repeat the extraction with an