Permeation of Water and Volatile Flavors through Packaging Films

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An experimental study has been carried out on the permeation of water and various flavors through packaging films used in commercial tobacco products. The permeation coefficients of these films were measured using a flow-type permeation system by means of steady-state transmission. The permeation coefficients of all the tested agents, including L-menthol, through three types of films could be systematically obtained over wide ranges of concentration and temperature. As the concentration of the tested agents in the upstream was increased, the permeation coefficients of water remained constant, while those of ethanol and the flavors increased. The concentration dependence of the permeation coefficients for ethanol and the flavors was caused by a plastic effect, leading to the structural loosening of the molecular chains of the films, and then markedly increased with an increase in the sorbed amounts of ethanol and the flavors on the films and decreased with an increase in temperature. The permeation coefficients of ethanol and the flavors mainly depended on their sorbed amounts by the films and governed by the affinity between the films and the flavors. Finally, a film having a polyvinylidene chloride or an aluminum layer was confirmed to be effective for depressing the permeation of ethanol and the flavors through them during storage.

Keywords: permeation, film, water, flavor, L-menthol

Undesirable permeation of flavors and water through packaging films has caused serious deterioration in the quality of products containing volatile compounds. Therefore, the permeation of various vapors through packaging films is of great commercial importance if the film is to be used as an effective barrier and has considerable theoretical interest. A number of papers have been published in relation to the permeation of vapors through various films. In these papers, several types of equipment have been used for the measurement of the permeation and diffusion as well as sorption by means of the transient response or the steady-state transmission (Rogers *et al*, 1960; Pasternak *et al*, 1970; Paul & Kemp, 1973; Shimoda *et al*, 1987a). Furthermore, Rogers *et al* (1960) and Takeuchi & Okamura (1976) published detailed studies regarding the contribution of sorption and diffusion on the permeation of several organic vapors in various polyethylene films over wide ranges of concentration. Other detailed studies in terms of the diffusion through the various films have also been published elsewhere (Frisch, 1957; Ayres *et al*, 1983). Salame & Steingiser (1977) predicted the effect of the chemical structure as well as the configuration of polymer molecules in the films on the permeation properties. For the food products, Shimoda *et al* (1987b) measured the permeation properties of volatile flavor compounds through packaging films.

In our previous studies (Miyauchi *et al*, 1995b, c, 1996), adsorption equilibria of various flavors and water for typical materials used in the boxes for tobacco products were summarized, and the migrations of water and flavors occurring inside stored packages were predicted based on their adsorption equilibria. However, the permeation coefficients

of volatile flavors and water through the packaging film used for tobacco products have not been measured systematically with regard to the conditions, i.e., temperature and concentration, and permeants as well as film properties. Especially, the permeation of L-menthol, which is commonly used for tobacco, chewing gum and candy, has not appeared in the literature. In addition, the measurements of permeation have a problem in that the structure of the polymer films leads to a serious swelling as flavors are largely sorbed on the films. Also, the concentration dependence of the permeation, which is one of the most important factors affecting the permeation rate, has not been reported quantitatively for volatile flavors.

The objectives of this study were (a) to measure the permeation coefficients of water and volatile flavors through the packaging films used for tobacco products, and (b) to investigate their dependences on the concentration, temperature, the properties of the flavors and the film components.

Experimental

Permeation measurement

Apparatus The permeation coefficient has been usually measured by the transient response or the steady-state transmission of the permeant through the film. Because the permeation coefficient has been found to be dependent on the permeant concentration in the polymer, the use of the steady-state transmission method under the condition of a constant concentration of the permeant has been recommended. A schematic drawing of the apparatus used for the steady-state permeation measurements is shown in Fig. 1. The main functions of the system are the control of gas flow-rates, the supply of volatile vapor at a constant concentration,
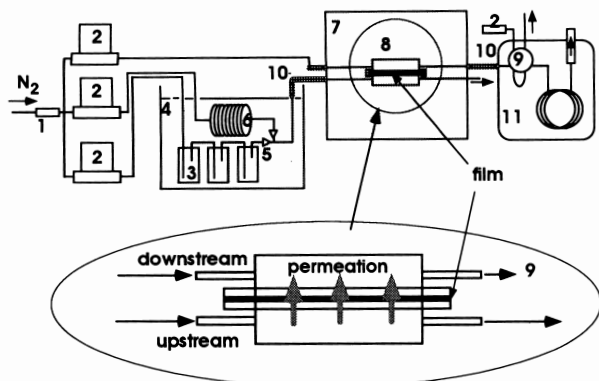
Fig. 1. Apparatus for steady-state permeation measurement. 1, dryer; 2, flow meter controller; 3, bubbler; 4, water bath; 5, valve; 6, heat exchanger; 7, air bath; 8, permeation cell; 9, six-way cock; 10, heater; 11, gas chromatograph (FID or TCD).

Fig. 2. Structure of films used in the experiments.

permeation through the film, and analysis of the vapor pressure permeating through it. Because the functions of system components and operating methods to supply the vapors were described in detail elsewhere (Miyauchi *et al.*, 1995a), only the devices concerning permeation and analysis are described in this paper.

A film was stretched, as shown in Fig. 1, across the flat surface of the permeation cell, and two compartments were placed at both sides of this film. The exposed surface area of the sample films, A or B, whose structures are shown in Fig. 2, was 0.0018 or 0.0057 m², respectively. Nitrogen containing the desired volatile agents was introduced into one of the compartments of the cell as an upstream gas. Dehumidified nitrogen was supplied the other compartment as a downstream gas. The upstream gas flowed at 1.7×10^{-6} m³/s, while the downstream flowed at a rate between 8.3×10^{-8} and 1.7×10^{-6} m³/s. The downstream concentration of the permeant was sufficiently small to be regarded as zero when compared with the upstream concentration. The permeation cell was placed in an air bath which was maintained at a constant temperature ranging from 293 to 313 K for water vapor, from 303 to 313 K for ethanol as well as flavor vapors, and at a constant temperature of 319 K for L-menthol vapor. In the downstream, the vapor pressures of water or the other agents which had permeated through the film were analyzed with a thermal conductivity detector (TCD) or a flame ionization detector (FID) of a gas chromatograph by operating a six-way cock or using a sampling tube, respectively.

Material Three typical films used for commercial tobacco products, shown as Samples A, B and C in Fig. 2, were selected and tested in the permeation measurements. Samples A and B were made mainly of polypropylene layers but Sample B was coated with a thin polyvinylidene chloride layer. Sample C consisted of nitrocellulose, polyethylene terephthalate, polyester, including an aluminum layer deposited by vacuum evaporation.

Several volatile agents that are generally known as major agents and used as flavors in tobacco production were selected as permeants in this study. The tested agents were water, ethanol, ethyl acetate, ethyl butyrate, D-limonene and L-menthol.
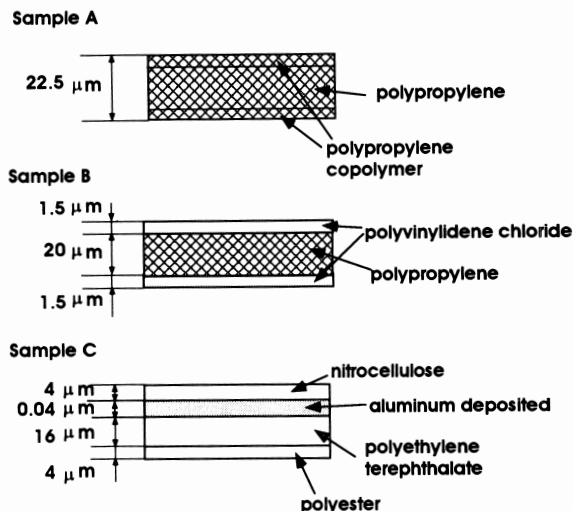
Procedure Adsorbed water exerts a negligibly small effect on the permeation or sorption of ethanol and flavors for the packaging films; therefore, the permeation of the pure volatile agent through them was studied.

The permeation coefficient (P) was measured based on the following equation,

$$Q=P\cdot(A/l)\cdot(p_u-p_d) \tag{1}$$

where Q, A, l, p_u and p_d are the rate of permeation, the exposed surface area of the film, the film thickness, and the upstream and downstream concentrations, respectively. The downstream concentration was measured after a steady-state permeation through the film had been achieved under the conditions of a constant upstream concentration. Because the downstream concentration was sufficiently small to be regarded as essentially zero in comparison with the upstream concentration, the permeation coefficient was calculated from the following equation introducing the Ideal Gas Law into Eq. (2),

$$P=\frac{Q}{(A/l)\cdot p_u}=\frac{p_d\cdot v\cdot l}{R\cdot T\cdot A\cdot p_u} \tag{2}$$

where v is the downstream flow rate.

Sorption measurement The apparatus used for the measurements of sorption was the same system mentioned in the previous study (Miyauchi *et al.*, 1995a). Each film reached equilibrium with the ethanol and flavor vapors at a constant temperature of 319 K for L-menthol or 303 K for the other agents. The times required to attain the equilibrium increased with the decreasing polar nature of the permeant. The maximum values were 6 h or 2 days for Samples A or B, respectively. The sorbed agent was desorbed by vacuum heating at a steady temperature of 373 K for 1 h, and the amount was then analyzed with a flame ionization detector (FID) of the gas chromatograph. The preliminary tests confirmed that these desorption conditions were adequate to ensure that the sorbed amounts of the agents could be measured accurately.
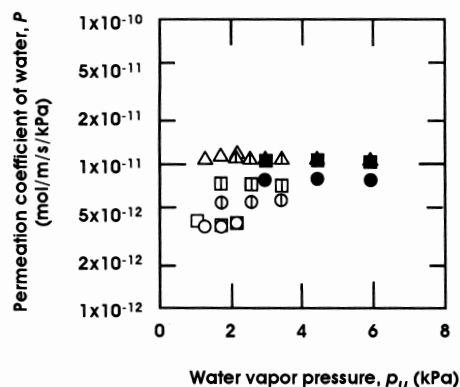
Fig. 3. Permeation coefficients of water. Sample A: ○, 293 K; ⊕, 303 K; ●, 313 K. Sample B: □, 293 K; ⊞, 303 K; ■, 313 K. Sample C: △, 293 K; ⊿, 303 K; ▲, 313 K.
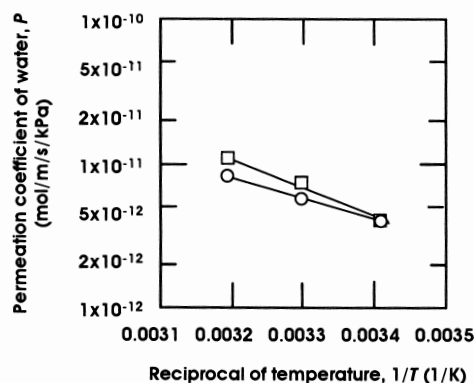

Fig. 4. Arrhenius plot of permeation coefficients of water. ○, Sample A; □, Sample B.

Results and Discussion

Water

Concentration dependence The permeation coefficient of water (P) was plotted against the upstream concentration, i.e., water vapor pressure (p), as shown in Fig. 3. The permeation coefficients were found to be almost the same order of magnitude and they were in particularly good agreement at a temperature of 313 K. For all types of film, the permeation coefficient was found to be almost constant, indicating a tendency to be nearly independent of the water concentration, as shown in Fig. 3. If products were sealed with each film, the water permeated through all types of film during storage. The permeated amounts of water were regulated to a specific level at the same environmental conditions of temperature and water-vapor concentration. These results indicate that the permeation of water through the films did not cause a modification of the film structures and that the diffusion coefficient of water was independent of the water concentration.

Temperature dependence The permeation coefficients for Samples A and B increased with an increase in temperature, and Arrhenius plots of ln P versus ($1/T$) gave a straight line, as shown in Fig. 4. The values of activation energy (E) for the permeation were obtained and listed in Table 1. On the other

Table 1. Activation energy for permeation.

Sample films	E [kJ/mol]				
	Water	Ethanol	Ethyl acetate	Ethyl butyrate	D-Limonene
A	27	64	59	62	98
B	38	115	149	184	140

hand, the permeation coefficient for Sample C slightly decreased with an increase in temperature (see Fig. 3). The difference in the temperature dependence of the permeation coefficient appeared to be attributed to the difference in the permeation mechanism indicated as follows: The former permeation is governed by the sorption and diffusion mechanisms of the permeant, while the latter is affected by the mechanism of Knudsen's flow, which is expressed by Eq. (3), through the capillary pores in an aluminum layer.

$$P_w = \sum \frac{4nr^3}{3RT} \cdot \left(\frac{2\pi RT}{M_w}\right)^{1/2} \tag{3}$$

where n and r are the number and radius of the pore, respectively. The permeation coefficient is expressed as a function of the square root of the reciprocal of the temperature, given as;

$$P_w = 1.92 \times 10^{-10} / \sqrt{T} \tag{4}$$

Therefore, the change in the permeation coefficient of Sample C with an increase in temperature, as mentioned above, can be explained in terms of Knudsen's flow.

Ethanol and flavors
Polypropylene film

Concentration dependence: For organic vapors, the permeation coefficient, which is expressed by Eq. (5), is known to correlate well with the experimental data for permeation through the polymer film and is a function of the permeant concentration (Rogers *et al.*, 1960).

$$P = P_0 \exp(\alpha p + \sigma c) \tag{5}$$

where P_0 is the value of the permeation coefficient as the concentration approaches zero and c is the sorbed vapor concentration. The values of α and σ indicate the concentration dependence factor of the permeation and sorption coefficients, respectively. In general, flavors have been applied to the products in the lower range of concentration. As expected, these isotherms of ethanol and flavors were found to obey Henry's Law in the low range of vapor pressure. The sorption isotherms of ethanol vapor for Samples A and B are shown in Fig. 5, and the obtained values of sorption coefficients (S), i.e., the slope of the isotherms, are listed in Tables 2 and 3. Takeuchi & Okamura (1976) reported similar behavior for the polyethylene films. Therefore, the concentration dependence factor (σ) of the sorption coefficients could be regarded as being zero, and then Eq. (5) becomes;

$$P = P_0 \exp(\alpha p) \tag{6}$$

The semilogarithmic plots of the permeation coefficients of ethanol against the ethanol vapor pressure are shown in Fig. 6. As can be seen from this figure, the permeation coefficient increased exponentially with an increase in the ethanol vapor pressure according to Eq. (6). As shown in Fig. 7, the plots of
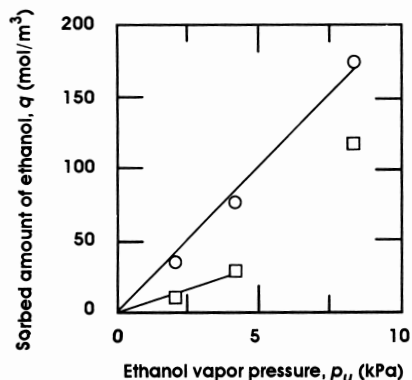
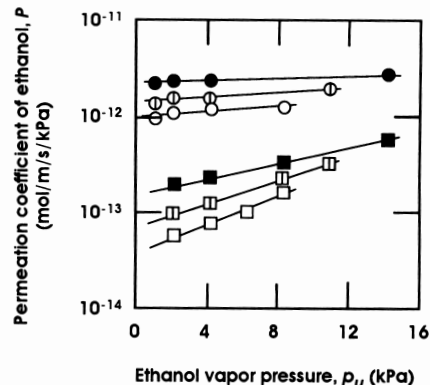**Fig. 5.** Sorbed amounts of ethanol for films. ○, Sample A; □, Sample B.

Fig. 6. Permeation coefficients of ethanol. Sample A: ○, 303 K; ⊕, 308 K; ●, 313 K. Sample B: □, 303 K; ⊞, 308 K; ■, 313 K.

Table 2. Permeation, sorption and diffusion parameters for Sample A.

Flavors	T [K]	P_0 [mol/ m/s/kPa]	α [1/kPa]	S [mol/ m³/kPa]	D_0 [m²/s]
Ethanol	303	9.9×10^{-13}	0.030	20	4.9×10^{-14}
	308	1.4×10^{-12}	0.030		
	313	2.2×10^{-12}	0.012		
Ethyl acetate	303	8.3×10^{-13}	0.25	32	2.6×10^{-14}
	308	1.3×10^{-12}	0.22		
	313	1.8×10^{-12}	0.28		
Ethyl butyrate	303	1.8×10^{-12}	0.98	144	1.2×10^{-14}
	308	2.4×10^{-12}	0.76		
	313	3.6×10^{-12}	0.67		
D-Limonene	303	1.5×10^{-12}	20	1353	1.1×10^{-15}
	308	3.8×10^{-12}	13		
	313	7.0×10^{-12}	9.7		
L-Menthol	319	2.5×10^{-11}	9.7	1701	1.5×10^{-14}

Table 3. Permeation and sorption parameters for Sample B.

Flavors	T [K]	P_0 [mol/m/ s/kPa]	α [1/kPa]	S [mol/m³/ kPa]
Ethanol	303	3.8×10^{-14}	0.17	6.3
	308	7.2×10^{-14}	0.14	
	313	1.6×10^{-13}	0.09	
Ethyl acetate	303	9.6×10^{-15}	0.74	18
	308	3.3×10^{-14}	0.74	
	313	6.3×10^{-14}	0.50	
Ethyl butyrate	303	1.4×10^{-15}	2.5	31
	308	4.2×10^{-15}	2.0	
	313	1.4×10^{-14}	1.8	
D-Limonene	303	—[a]	—[a]	288
	308	1.1×10^{-16}	16	
	313	2.5×10^{-16}	14	
L-Menthol	319	1.3×10^{-13}	20	1497

[a] The permeated amount was too small to detect the rate of permeation.
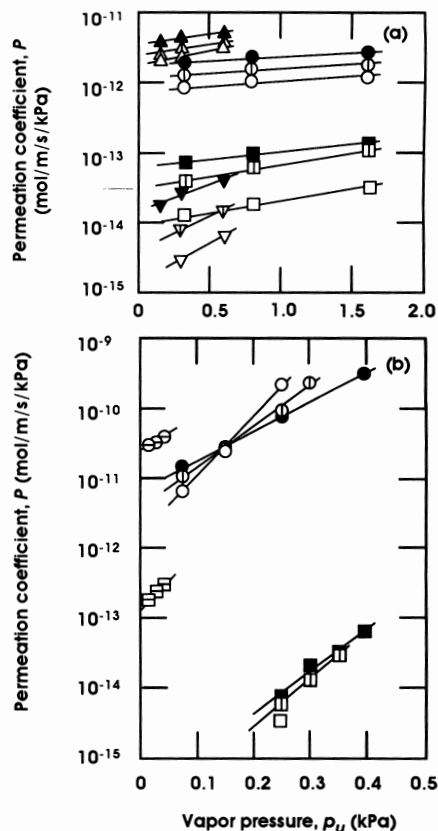

Fig. 7. Permeation coefficients of flavors. (a) ethyl acetate—Sample A: ○, 303 K; ⊕, 308 K; ●, 313 K; Sample B: □, 303 K, ⊞, 308 K, ■, 313 K. ethyl butyrate—Sample A: △, 303 K; ▲, 308 K; ▲, 313 K; Sample B: ▽, 303 K, ▼, 308 K, ▼, 313 K. (b) D-limonene—Sample A: ○, 303 K; ⊕, 308 K; ●, 313 K; Sample B: □, 303 K, ⊞, 308 K, ■, 313 K. L-menthol—Sample A: ⊖, 319 K; Sample B: ⊟, 319 K.

permeation coefficients against the concentration for all the flavors demonstrated behavior similar to that of ethanol. These results suggested that the permeation for both ethanol and flavors could be explained by the same mechanism. The values of permeation and sorption parameters of ethanol and flavors for the Samples A and B are listed in Tables 2 and 3, respectively. For organic vapors, it was known that the adsorbed agent takes part in plasticizing of the film, leading to a molecular structural loosening of the film (Prager & Long, 1951). To investigate the plasticizing effect on the permeation, the values of α were plotted against the sorption coefficients in Fig. 8. The values of α, which indicated the concentration dependence factor of the permeation coefficient, were found to increase with an increase in the sorption coefficient. These results lead to the conclusion that this plasticizing effect increased with the sorbed amounts of
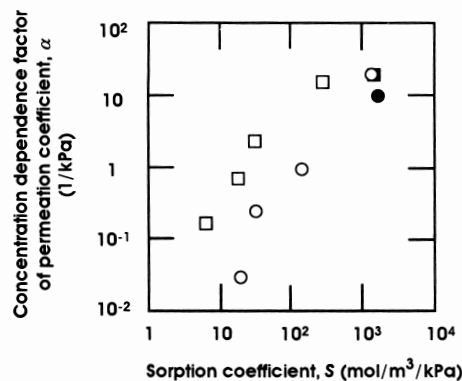
Fig. 8. Effect of concentration dependence factor of permeation coefficient on sorption coefficient. Sample A: ○, 303 K; ●, 319 K; Sample B: □, 303 K; ■, 319 K.

flavors.

Temperature dependence: Arrhenius plots, in the same manner as in Fig. 4, provided the values of the activation energy (E) for permeation and are listed in Table 1, using the values of P_0 extrapolated to the concentration of zero. Because the slope of linear regression curves for permeation coefficient was found to decrease with an increase in temperature as shown in Fig. 6, the temperature dependence of the permeation coefficient, i.e., E, decreased with an increase in the permeant concentration. Aitken & Barrer (1955) explained that for an analogous phenomenon, the loosening molecular chains of the film increased so much at the higher temperature that the increment of the adsorbed agent produced a lower plasticizing effect in the polymer. Therefore, similar behavior is considered to take place, providing these measured values. In particular, in a comparison under the condition of the same vapor pressure, the permeation coefficient was found to decrease with an increase in temperature in the higher vapor pressure range of D-limonene.

Effect of permeant properties: The permeation coefficients are known to be dependent on two different factors: a diffusion term governed by the size of the permeant, and a sorption term attributed to the affinity between the film and the permeant. The sorption coefficient increased in the order: ethanol<ethyl acetate<ethyl butyrate<D-limonene; this corresponds to a decrease in the polar nature of the permeant, because the tested films have a less polar nature. On the other hand, the mean diffusion coefficient (D) of a given permeant is calculated from the following relationship.

$$D = P/S \qquad (7)$$

The diffusion coefficient at a concentration of zero (D_0) then has the same physical meaning as the molecular diffusion for an infinitely diluted liquid solution in the case of diffusion in liquid (Takeuchi & Okamura, 1976). Considering the concentration dependence of the permeation coefficient, the values of D_0 can be calculated by extrapolating the values of D to a concentration of zero and are listed in Table 2. The calculation was based on the assumption that the Sample A film was a homogenous polypropylene film. The obtained values of D showed an equal order of magnitude to those for the polypropylene film reported by Ikegami *et al.* (1988).

Therefore, the diffusion rate of the permeant through Sample A was found to be limited mainly by the rate through the polypropylene layer. The diffusion coefficient obtained increased in the order: D-limonene<ethyl butyrate<ethyl acetate<ethanol, leading to the conclusion that the diffusion coefficient increased with a decrease in the molecular size of the permeant, as expected. Within the concentration range measured, the permeation coefficient for Sample A increased in the order: ethanol as well as ethyl acetate<ethyl butyrate< D-limonene in the same order as mentioned above for the sorption coefficient, but in the opposite order for the diffusion coefficient. Therefore, the effect of permeant properties on the permeation coefficient was found to be mainly dependent on the sorption, which, in turn, is governed by the affinity between the film and the permeant.

Comparison with different types of films: Polyvinylidene chloride film has been widely used in commercial products to prevent flavor loss in stored foods. As shown in Figs. 6 and 7, the permeation coefficients of ethanol and flavors for Sample B, are several orders of magnitude smaller than those for Sample A, demonstrating the lessening effect of the polyvinylidene chloride layer on the flavor permeation. Because flavors have been applied in the lower ranges of concentration in tobacco products, no marked permeation of flavor through Sample B is detected in commercial products. Determination of the greatest amounts of flavors which could permeate through Sample B was then attempted, assuming that the tobacco products were stored under the highest concentration level of flavors and the highest temperature in Japanese marketing; tobacco products containing 100 mg of L-menthol were stored for 1 month at a temperature of 319 K. As a result, the estimated amount was assessed to be about 1 mg, which was regarded as a negligible amount for smoke odor and taste. Therefore, the use of this film as an outer packaging is suitable for minimizing flavor losses during storage. As shown in Tables 2 and 3, the sorption coefficients for Sample B were found to be smaller than those for Sample A. Koros *et al.* (1982) explained that the improvement of barrier properties brought about a decrease in permeant sorption by treating the surface of film with fluorine. A similar effect was found to be caused by coating the surface with the polyvinylidene chloride layer.

Because the permeation of flavors through Sample C, i.e., the film having a deposited aluminum layer, was at an extremely low level, the values of the permeation coefficient were less than the minimum measurable with the gas chromatograph, which corresponds to 10^{-15} mol/s/m/kPa. The permeation through this film was considered to be governed by Knudsen's flow through the capillary pores existing in the aluminum layer, as mentioned earlier. Because ethanol and flavors have a relatively large molecular size, no permeation of them through these capillary pores was observed, as expected.

Finally, the polyvinylidene chloride or aluminum layer with a thickness of 3 or 0.04 μm, respectively, could be seen to be effective for conserving the flavor within the package.

Nomenclature

A = exposed surface area of films ⟶ [m^2]

c=sorbed vapor concentration $[mol/m^3]$
D=diffusion coefficient $[m^2/s]$
E=activation energy $[J/mol]$
l=film thickness $[m]$
M=molecular weight $[kg/mol]$
n=pore number in aluminum layer $[-]$
P=permeation coefficient $[mol/m/s/kPa]$
p=concentration (=vapor pressure) upstream $[kPa]$
Q=rate of permeation $[mol/s]$
q=sorbed amount $[mol/m^3]$
R=gas constant $[J/K/mol]$
r=pore radius in aluminum layer $[m]$
S=sorption coefficient $[mol/m^3]$
T=temperature $[K]$
α=concentration dependence factor of permeation
    coefficient $[1/kPa]$
σ=concentration dependence factor of sorption
    coefficient $[m^3/mol]$

<Subscripts>

d=downstream
u=upstream
0=concentration approaching zero

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