

Binary Adsorption Equilibria of Various Flavors and Water for Materials Contained in a Box of a Tobacco Product

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An experimental study has been carried out on the binary adsorption equilibria of various flavors and water for typical materials used in a box of a tobacco product. A flavor component of L-menthol, which was sublimated from the solid state, was found to be adsorbed onto the surfaces of each material without phase re-transition under its unsaturated condition. For tobaccos, papers and filters, flavors with a water soluble or polar nature were adsorbed to a greater degree than otherwise, while for the activated carbons, this dependence showed the opposite tendency except for L-menthol. These behaviors of the binary adsorption equilibria of various flavors and water are explained as follows; (a) for the tobacco and paper, the flavors were mainly adsorbed by the solution in the adsorbed water, and to some extent, on the hydrophobic sites of the material's surface, (b) for the filter, they were adsorbed on the hydrophobic sites such as the acetyl group inside the tow, (c) for activated carbon, their adsorption was attributed to the filling of flavor molecules in the inner surface of the micropores, but depended on their size.

Keywords: tobacco product, activated carbon, ethyl butyrate, L-menthol, D-limonene, water, binary adsorption

Various volatile flavors are playing an increasingly important role in the enhancement of taste and odor of food and tobacco products. However, a number of these volatile compounds is widely recognized as being transferred inside the package, depending on the adsorption equilibrium.

Various methods have been proposed to predict the effects of the physical properties of adsorbates on their adsorption; Reucroft *et al.* (1971) reported that the constant values of the Dubinin-Astakhov (DA) equation which was applied to the activated carbons were estimated using electric polarization. Matsui *et al.* (1992) found that the sorption of flavors into various packaging films could be predicted by an affinity concept derived from the solubility parameter values of these materials. This concept represents the interaction forces acting between the flavor molecules and the films. Samejima (1983) reported that for tobacco leaves the adsorption equilibria of flavors were affected by the number of carbon atoms as well as by the functional groups. Wilson (1993) explained that after reaching equilibrium, the distribution of L-menthol contained in the tobacco column and filter tip was related to the solubility parameter values of both materials. Miyauchi *et al.* (1995b, c) measured the binary adsorption equilibria of ethyl acetate and water for typical materials used in the box of the tobacco product. The flavors were then found to migrate from the tobacco column to the filter tip, while water transfers backwards during storage and marketing. However, the binary adsorption equilibria of various flavors and water for tobacco and its packaging materials have not been systematically measured and especially the adsorption phenomena of L-menthol, which exists in a solid or vapor state at the temperature of 303 K, have not appeared in the literature.

The objectives of this study were to (a) clarify the phase

state of L-menthol contained in the box of the tobacco product and (b) summarize the effect of the physical properties of various flavors on the binary adsorption equilibria of flavors and water for typical materials contained in a box of a tobacco product.

Experimental

Materials Tobacco, paper, filter, tow and activated carbon were used as typical materials contained in a box of the tobacco product. The tow is the cellulose acetate fiber which forms the filter. From measurements of nitrogen adsorption, the specific volumes of micropores (v_p) for coconut activated carbon or that contained in the filter were determined to be 0.43 and 0.22 cm³/g, respectively. Most of their pores had radii of less than 1 nm, which are referred to as micropores and in this range of pore radii it is known that the capillary condensation which was applied to the Kelvin equation does not take place as a mechanism of adsorption (Urano, 1975).

Several flavors such as ethyl acetate, ethyl butyrate, D-limonene and L-menthol were selected based on the consideration of their solubility in water as well as the phase state. Their solubility in water was measured with a gas chromatograph (GC) and are listed in Table 1. The values of radius r of a given flavor molecule, as listed in Table 1, was calculated from the following equation by assuming that molecules were arranged in a face-centered close packing configuration in the liquid state (Keii, 1965).

$$r = \left(\frac{M}{4\sqrt{2} \cdot N_A \cdot \rho} \right)^{1/3} \quad (1)$$

This radius has been used for determining the specific surface area of the porous material (Keii, 1965) and diffusion rate in

polymers (Takeuchi & Okamura, 1976).

Determination of the phase state of L-menthol Since a differential scanning calorimeter (DSC) has been used in the studies of the phase state (Kugimiya & Donovan, 1981; Gekko & Satake, 1981; Nakazawa *et al.*, 1985; Roos, 1986), the phase state of L-menthol could be determined by measuring its endotherm, i.e., the latent heat of melting, with the DSC. Thus the DSC (Seiko Instruments Inc. Model DSC220C) was used to measure the thermograms of bright yellow, Burley tobaccos and the filter. Before the DSC measurements, each material was conditioned at a constant temperature of 303 K and at a vapor pressure of water and L-menthol corresponding to $p_w/p_w^0=0.6$ and over $p_t/p_t^0=0.6$, respectively. Six mg samples of material was placed in hermetic aluminum pans and used for the DSC measurement, while an empty pan was used as the reference sample. Thermograms were obtained at a constant heating rate of 20 K/min over the temperature range of 293–393 K which included the melting point of 316 K for L-menthol.

Measurements of vapor-liquid adsorption equilibrium

Table 1. Physical properties of flavors.

Flavor	Solubility in water, s_w [wt%]	Radius, r [nm]
Ethyl acetate	7.1 (303K)	0.31
Ethyl butyrate	0.7 (303K)	0.34
L-menthol	0.5 (319K)	0.37
	0.04(303K)	
D-limonene	0.01(303K)	0.36

The apparatus used for the measurements of adsorption was the same system mentioned in a previous study, i.e., a flow-type multi-component adsorption system (Miyachi *et al.*, 1995a). Since the removal of the intrinsic volatile compounds and any adsorbed vapor was required to get reproducible values of adsorption equilibria, the materials were pre-treated by vacuum drying under the conditions listed in Table 2. Before measurement, each material was held in equilibrium with a constant vapor pressure of pure water, $p_w=2.5$ kPa, corresponding to $p_w/p_w^0=0.6$. During the measurements, the sample was kept in the adsorption cell until it reached equilibrium with the desired mixtures of flavor and water vapor at a constant temperature of 319 K for

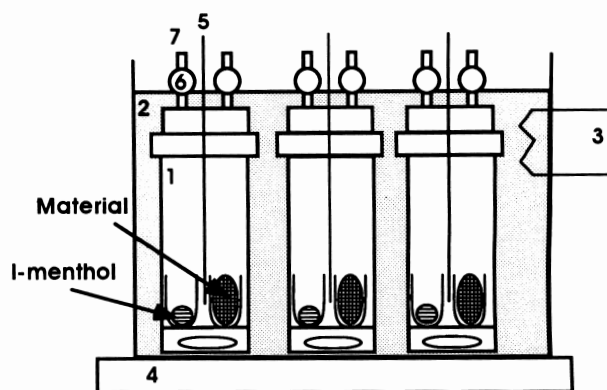


Fig. 1. Closed-type adsorption cells for L-menthol. 1, cell; 2, water bath; 3, heater; 4, magnetic stirrer; 5, thermocouples; 6, valve; 7, sampling port.

Table 2. Experimental conditions.

Materials	Pre-treatment (K, min)	Desorption (K, min)			
		Water	Flavor	L-menthol	
Tobacco	353, 480	363, 60	403, 60	453, 150	
Paper	373, 480	403, 60	403, 60	403, 90	
Filter	373, 480	403, 60	403, 60	403, 150	
Activated carbon	473, 480	473, 180	473, 180	473, 180	
Gas chromatograph conditions					
	Water	Ethyl butyrate	D-limonene	L-menthol	
For adsorption					
Column (ID)	2 mm×1 m	3 mm×3 m	3 mm×3 m	3 mm×3 m	
Liquid phase	Porapak Q	PEG20	PEG20	PEG20	
Detector	TCD	FID	FID	FID	
Flow rate (ml/min)	50	80	80	80	
Temperature					
Oven (K)	413	373	393	433	
Detector (K)	503	503	503	503	
For analysis					
Column (ID)	0.53 mm×30 m	0.25 mm×30 m	0.25 mm×25 m	0.53 mm×30 m	
Liquid phase	GS-Q (J & W)	DB-WAX (J & W)	ULTRA-1 (HP)	DB-WAX (J & W)	
Detector	TCD	FID	FID	FID	
Flow rate (ml/min)	3	1	1	6.5	
Temperature					
Oven initial (K)	433	308	343	353	
		(Hold 5 min)			
rate (K/min)		5	2	2	
final (K)		473	503	503	
Injection (K)	503	503	523	503	
Detector (K)	523	523	573	523	

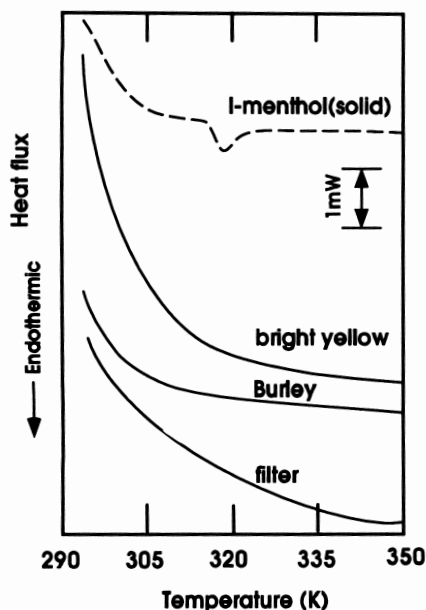


Fig. 2. DSC curves for L-menthol adsorbed tobacco and filter.

L-menthol or 303 K for the other flavors. The adsorbed water and flavor were desorbed by vacuum heating and then their amount was analyzed using a thermal conductivity detector (TCD) or a flame ionization detector (FID) for the gas chromatographs, respectively, in the same manner mentioned in a previous study (Miyachi *et al.*, 1995b). The times required to attain the equilibrium increased with decreasing solubility of the given flavors in water. The maximum value was 2 days for L-menthol or D-limonene. The desorption and GC conditions are listed in Table 2. The adsorbed amounts of the pure component were obtained based on the weighing method (Miyachi *et al.*, 1995a). Because the adsorbed amounts of L-menthol and D-limonene on the activated carbon could not be measured accurately, they were determined by subtracting the adsorbed amounts of water obtained by the desorption method from their total amounts measured by the weighing method.

Measurements of vapor-solid adsorption equilibrium

It was impossible to control the constant vapor pressure of L-menthol at a temperature of 303 K with the flow-type adsorption system, because the solid L-menthol could not be stably sublimated and the condensation or crystallization took place at the corner of the system's connecting pipe. Therefore, a closed-type adsorption cell, which is illustrated in Fig. 1, was prepared and used to measure the vapor-solid adsorption equilibrium. The cell (1) was made of stainless steel with about a 2 l inner volume. To reduce the time required to attain equilibrium, a magnetic stirrer (4) was equipped to force air circulation within the cell. The cells containing both materials tested and the solid L-menthol were immersed in a water bath (2) controlled by the heater (3) at the constant temperature of 303 K. The temperature of the cells was monitored with K-type thermocouples (5). The preliminary tests confirmed that the adequate time required to attain equilibrium was over 3 or 4 weeks for the tobacco or filter, respectively. Each material was kept at a constant

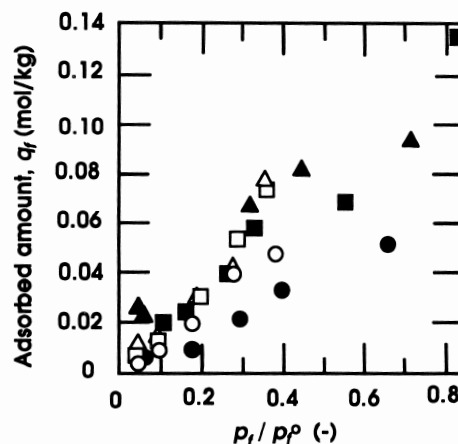


Fig. 3. Adsorbed amounts of L-menthol. Vapor-liquid system (319 K): ○, bright yellow tobacco; □, Burley tobacco; △, filter. Vapor-solid system (303 K): ●, bright yellow tobacco; ■, Burley tobacco; ▲, filter.

temperature of 303 K and $p_w/p_w^0=0.6$, and the loading and unloading of the samples into/out of the cells were carried out in an air-conditioned room at a temperature of 295 K and $p_w/p_w^0=0.6$. The amounts of L-menthol adsorbed onto the materials were determined by the desorption method as previously mentioned. Those in the vapor phase were obtained after subtracting those found on the materials from the total loading amounts. The vapor pressure of L-menthol was then calculated using the ideal law. Therefore, the amount of L-menthol adsorbed onto the material was found to be on an equal order of magnitude as that in the vapor phase in order to obtain reproducible results. So, the conditions of the loading amounts were chosen by utilizing the adsorption equilibrium that had been obtained with the flow-type system.

Results and Discussion

Adsorption equilibrium of L-menthol in vapor-solid or vapor-liquid system

The DSC thermograms of various tobaccos and a filter in vapor-solid equilibrium with L-menthol is shown in Fig. 2, compared with that of the pure solid of L-menthol shown by the broken curve. The curves for all samples were adjusted using 0.06 mg of L-menthol as the base. The melting transition of L-menthol as a solid gave an endotherm peak near 316 K. However, no peak appeared in the curves for L-menthol adsorbed on all the materials. The peak disappearance was considered to be caused by the relatively greater adsorption force between a flavor molecule and material surfaces. This result leads to the conclusion that L-menthol was not deposited in its solid state without a phase re-transition under its unsaturated condition. Therefore, the phase re-transition or formation of an adsorbate solid during the adsorption process of the sublimated vapor onto the surface of the material is considered to be necessary for the nucleation formation of the adsorbate, as is well known from crystal studies. Therefore, the adsorption equilibrium of L-menthol should be investigated in both the vapor-solid as well as the vapor-liquid system.

As shown in Fig. 3, the adsorption equilibria of L-menthol

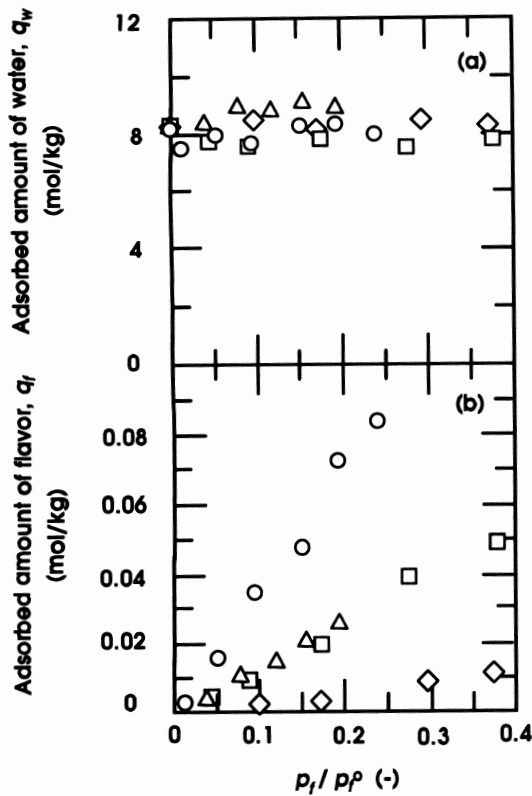


Fig. 4. Adsorbed amounts of (a) water and (b) flavor for bright yellow tobacco. \circ , ethyl acetate; \triangle , ethyl butyrate; \square , L-menthol (319K); \diamond , D-limonene.

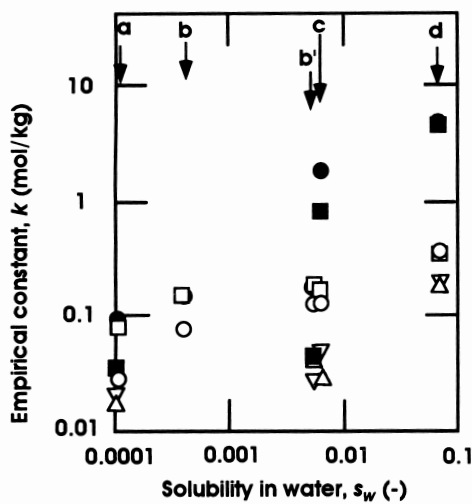


Fig. 5. Effect of the solubility in water on the adsorption equilibria of flavors for tobaccos, papers and filters. Materials: \circ , bright yellow tobacco; \square , Burley tobacco; \triangle , cigarette paper; ∇ , label (hard); \bullet , filter; \blacksquare , tow. Flavors: a, D-limonene; b, L-menthol (303K); b', L-menthol (319K); c, ethyl butyrate; d, ethyl acetate.

are represented in the vapor-liquid and the vapor-solid systems. For tobaccos and filters, the amount of L-menthol adsorbed in the vapor-solid system is almost as great as that in the vapor-liquid system. Therefore, no significant difference essentially exists between the behaviors of the adsorption equilibria based on either vaporization or sublimation. However, the small difference in the observed adsorption

Table 3. Chemical composition of tobaccos (Nakanishi & Kobari, 1989).

Components	Bright yellow	Burley
Protein and amino acids	0.152	0.271
Organic acids	0.124	0.141
Tannin	0.022	0.029
Inorganic material	0.135	0.165
Reducing sugars	0.225	0.012
Crude fiber	0.135	0.147
Pectin	0.079	0.082
Ether-soluble material	0.073	0.071
Unidentified	0.056	0.082

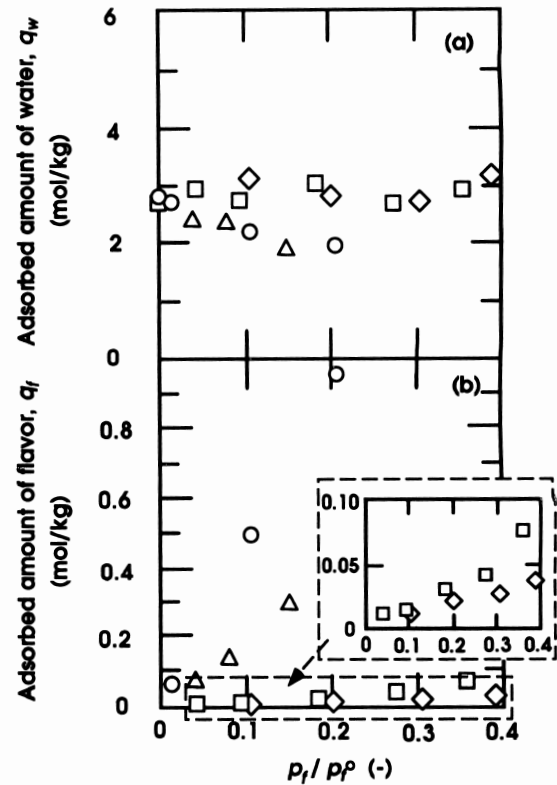


Fig. 6. Adsorbed amounts of (a) water and (b) flavor for filter. \circ , ethyl acetate; \triangle , ethyl butyrate; \square , L-menthol (319K); \diamond , D-limonene.

equilibria was explained in terms of the different temperatures in measuring or the heat of adsorption between both conditions.

Binary adsorption equilibria

Tobacco and Paper It was found that for tobacco and papers, ethyl acetate was mainly adsorbed by a solution mechanism into the adsorbed water (Miyachi *et al.*, 1995b). Therefore, the difference in the chemical potential of the solution is given as a function of temperature and relative pressure according to Henry's law. Thus, it might be expected that the adsorbed amount of the given flavors would depend on their relative pressure under the condition of constant temperature. However, since the vapor-liquid equilibria of the studied system are unknown, the activity coefficient could not be taken into consideration. The adsorbed amounts of water (q_w) and flavor (q_f) for bright yellow tobacco were plotted versus the ratio of the vapor pressures of the flavors to their pure saturated vapor (p_i/p_i^0) in Fig. 4. The results show that

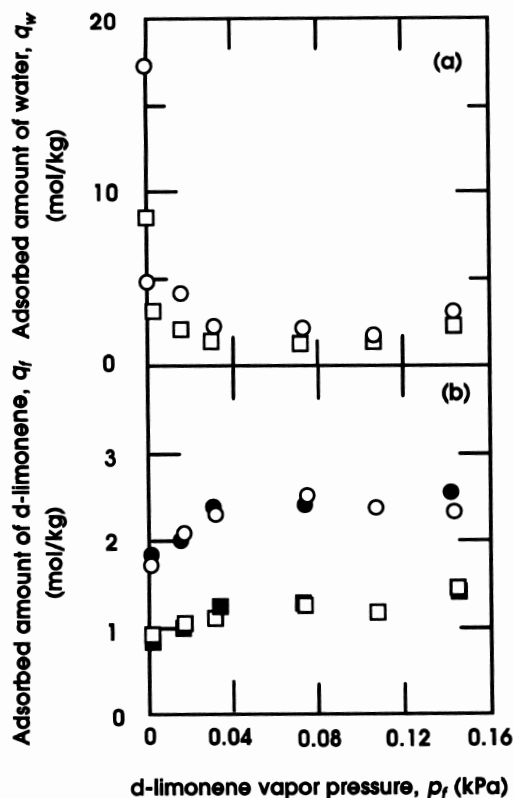


Fig. 7. Adsorbed amounts of (a) water and (b) D-limonene for activated carbons. Binary adsorption: \circ , coconut; \square , coconut in filter. pure adsorption: \bullet , coconut; \blacksquare , coconut in filter.

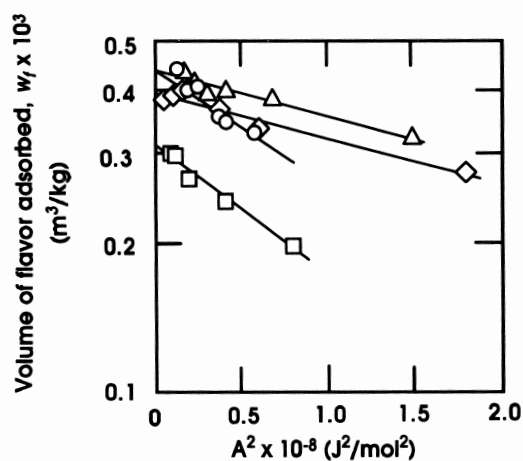


Fig. 8. Dubinin plots of adsorbed amounts of flavor for activated carbon. \circ , ethyl acetate; \triangle , ethyl butyrate; \square , L-menthol (319K); \diamond , D-limonene.

for all the given flavors, q_w was nearly constant, while q_t proportionally increased with increasing p_t/p_t^0 , which can be expressed in terms of the following equation,

$$q_t = k \times \left(\frac{p_t}{p_t^0} \right) \quad (2)$$

where k is an empirical constant, indicating the same behavior for the ethyl acetate and water system (Miyachi *et al.* 1995b). Also the adsorbed amount of the flavor (q_t) was found to increase with their increasing solubility in water (s_w) as shown in Fig. 5. The values of k for various tobaccos and

Table 4. Empirical constants for activated carbons.

Flavor	w_t^0 [cm^3/g]		E [kJ/mol]	
	Coconut	Coconut in filter	Coconut	Coconut in filter
Ethyl acetate	0.44	0.26	14.2	12.4
Ethyl butyrate	0.44	0.25	22.1	22.5
L-menthol (319K)	0.28	0.12	13.2	16.0
D-limonene	0.40	0.20	21.9	22.0

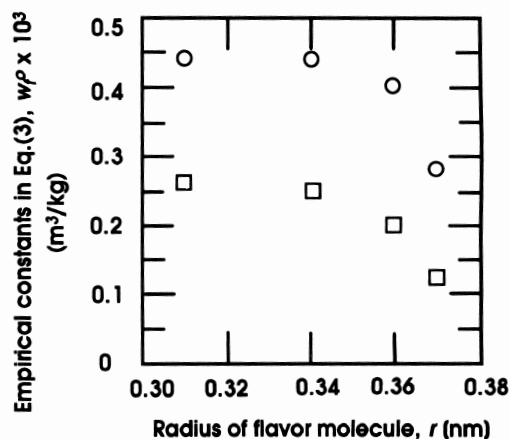


Fig. 9. Correlation between the radius of flavor molecule and the w_t^0 constants for activated carbons. \circ , coconut; \square , coconut in filter.

papers could be expressed in terms of s_w , as expected from the aforementioned adsorption characteristics.

The values of k for flavors having poor water solubility showed a remarkably small value without approaching the value of zero. Furthermore, the values of k obtained from D-limonene given by Burley tobacco was almost three times greater than that by the bright yellow tobacco, while those obtained from the water-soluble flavor, i.e., ethyl acetate, given by both tobaccos were in good agreement. These results indicated that one factor which affects the flavor adsorption, albeit a small amount, is bonding on the surface of the material. To investigate the adsorption sites of tobaccos using poor water-soluble flavors, i.e., L-menthol, the adsorption equilibrium for the cell wall materials such as crystal cellulose, pectin, and lignin were carried out. Although the obtained data were not presented in this paper, the results showed that the values of k for cell wall materials are an order of magnitude smaller than those for tobaccos. Also, because small fluctuations in the value of q_w were observed as previously mentioned, their adsorption was recognized to take place at the sites where water was not adsorbed. Here, the chemical composition of tobaccos are listed in Table 3 (Nakanishi & Kobari, 1989). This lead to the consideration that the adsorption sites are hydrophobic ones of protein, amino acids, etc.

Filter In order to compare the adsorption equilibria of tobacco with that of the filter, the amounts of q_w and q_t of given flavors and water for the filter were plotted versus the ratio (p_t/p_t^0), as shown in Fig. 6. The values of q_w for esters, such as ethyl acetate and ethyl butyrate, slightly decreased with an increase in p_t/p_t^0 , while q_w for the other flavors was

almost constant. For all flavors, the values of q_f proportionally increased with an increase in p_f/p_f^0 . The values of k calculated for the filter and tow were plotted as closed symbols in Fig. 5. It was found that the values of k for the tobaccos and papers increased continuously with increasing s_w over the whole range of s_w , but those for the filter and tow changed discontinuously when s_w was changed from L-menthol (319 K) to ethyl butyrate. This result leads to the conclusion that the flavor adsorption of the filter and tow was caused not by solution in the adsorbed water but rather by adsorption on the hydrophobic sites of the acetyl group of the tow and filter, as has been reported for ethyl acetate (Miyachi *et al.*, 1995b).

For the application of flavors such as ethyl butyrate, D-limonene, L-menthol having a poor water-soluble or nonpolar nature, it should be noted that the value of q_f for the tow was remarkably different from that for the filter. Curran (1975) reported the same behavior regarding L-menthol. During the filter molding process, triacetin is added to the tow and then a part of the tow is melted and reformed. The adsorption characteristics of triacetin were considered to be the same as that of tow (Wilson, 1993). The adsorbed amount of D-limonene for a mixture of triacetin and tow are larger than that for triacetin. On the other hand, Matis (1983) and Best (1993) proposed that flavors are deeply adsorbed inside the tow during storage. In addition, Halek & Meyers (1989) reported that a sorption study of D-limonene for polyethylene having a low density was caused not only by surface attraction but also by matrix dissolution. Therefore, these results suggested that the amount adsorbed in the melted and reformed part inside the tow would be greater than that on the outside surface of the tow.

Activated carbon Typical binary adsorption equilibria of poor a water-soluble or nonpolar flavor for the activated carbons are shown in Fig. 7, compared with those obtained from the adsorption of pure vapor. All the given flavors were substituted for some adsorbed water in the micropores or were adsorbed onto them. On the other hand, the effect of adsorbed water on the flavor adsorption was negligible, indicating the same behavior as in the ethyl acetate and water system (Miyachi *et al.* 1995b). The constants of E and w_f^0 contained in the following equation were calculated by applying a regression analysis to the experimental data;

$$w_f = w_f^0 \exp\left(-\left(\frac{A}{E}\right)^n\right) \quad (3)$$

$$w_f = \frac{q_f \times M}{\rho} \quad (4)$$

where w_f^0 is the volume of the micropores and A is the adsorption potential [= $RT \ln(p_f/p_f^0)$]. The recommended value of n is 2 for the organic solvent adsorption of activated carbon. In Fig. 8, the experimental data for all the given flavors were plotted versus the square of the adsorption potential (A^2) in Fig. 8. The regression lines obtained by applying the DA equation appeared to fit well and then the empirical constants of E and w_f^0 are listed in Table 4. Except for L-menthol, the obtained constants of E indicated a tendency to increase with decreasing value of s_w or polar nature. This suggests that the adsorption equilibria for activated carbon were mainly affected by dispersion forces.

The different behavior of L-menthol was explained in terms of the structural nature of the molecule in the hydroxyl groups. Since the values of w_f^0 seem to be related to the size of the flavor molecule, they were plotted versus their radius r as shown in Fig. 9. It is found that the values of w_f^0 for given flavors decrease with an increase in r , while those having a small r agree with the v_p obtained from nitrogen adsorption. This decrease in w_f^0 is thought to be caused by steric hindrance, which also occurred during a catalytic study (Niwa *et al.*, 1984).

Finally, comparing E and w_f^0 for both activated carbon, it was found that E for coconut in the filter was almost the same as that for the new coconut, while w_f^0 for the former activated carbon was half than that for the latter one. Therefore, the added triacetin results in decreasing the volume for adsorption by filling the micropores of the new activated carbon.

Nomenclature

A	=free energy of adsorption	[J/mol]
E	=characteristic free energy of adsorption	[J/mol]
k	=constant in Eq. (2)	[mol/kg/kPa]
M	=molecular weight	[kg/mol]
N_A	=Avogadro's number	[-]
n	=constant in Eq. (3)	[-]
p	=vapor pressure	[Pa]
p^0	=saturated vapor pressure	[Pa]
q	=amount of adsorbed component	[mol/kg-dry material]
R	=gas constant	[J/K/mol]
r	=radius of molecule	[nm]
s_w	=solubility in water	[-]
T	=temperature	[K]
v_p	=micropore volume	[m ³ /kg]
w	=volume of adsorbed component	[m ³ /kg]
w_f^0	=constant in Eq. (3) (=micropore volume)	[m ³ /kg]
ρ	=density	[kg/m ³]
<Subscripts>		
f	=flavor	
w	=water	

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