

**BINARY ADSORPTION ISOTHERMS OF WATER AND ETHYL
ACETATE VAPOR FOR MATERIALS
CONTAINED IN A BOX OF A TOBACCO PRODUCT**

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ABSTRACT

An experimental study has been carried out on the characteristics of binary adsorption isotherms of water and volatile flavor for typical materials used in a box of a tobacco product or cigarettes. Ethyl acetate was chosen as a model for water-soluble volatile flavor. Binary adsorption isotherms for the tobacco, papers, filters, and activated carbons were measured with a flow-type multi-component adsorption system under the constant conditions of temperature at 303 K and vapor pressure of water at 2.5 kPa in the vapor pressure range of ethyl acetate from 0 to 4.2 kPa. A linear equation was applied to express the binary adsorption isotherms for the tobacco, papers and filters, while a Dubinin-Astakhov equation was applied for the activated carbons. The binary adsorption was characterized into three groups, depending on the selectivity as well as the mechanism of adsorption; i.e. (1) for tobacco and papers, water was adsorbed much greater rather than ethyl acetate, (2) for filters, ethyl acetate was adsorbed on the surface as great as water, (3) for activated carbons, ethyl acetate was adsorbed much greater onto their micropores rather than water. The results showed that ethyl

acetate migrates from the tobacco column to the filter tip, while spontaneously water moves backward.

INTRODUCTION

The current tastes in cigarettes show a tendency towards lower contents of nicotine and tar. However, the volatile flavors play an important role in maintaining the conventional taste even though the contents of nicotine and tar are reduced. In the future, the enhancement of smoke odor and taste by using the volatile flavors will play an increasing important role in the manufacturing process and the design of quality. At present, the application of volatile flavors to tobacco is performed in a rotary drum mixer by spraying a mixture of alcohol and various volatile flavors on the shredded tobacco leaves maintaining their equilibrium moisture content (EMC) at a relative humidity of 60 %. The sprayed liquid contains 99 wt% alcohol and each flavor of up to 100 ppm. Therefore, the adsorption isotherms are desired for each volatile flavor in the lower range of their vapor pressures.

Although simulation models of flavor migration for the non-charcoal filter or plain filter product have been presented⁽¹⁾⁽¹¹⁾, the behavior for the single component of flavor was treated in these papers. Nakanishi et al.⁽⁶⁾ and Samejima⁽⁸⁾ pointed out that the adsorbed water exerts a great influence on the adsorption phenomena of the flavors, and then not only the pure adsorption of the flavors but also the binary adsorption of a mixture of water and flavors must be studied. Okazaki et al.⁽⁷⁾ and Nakanishi et al.⁽⁶⁾ reported the binary adsorption equilibria of water and organic solvents for activated carbon and tobacco, respectively. However, the binary adsorption isotherms of water and flavors for tobacco and its packaging materials have not been measured systematically and the information on the prediction of migration for water as well as flavors has not appeared in the literature.

The objectives of this study were (a) to measure the binary adsorption isotherms for typical materials contained in a box of a tobacco product under the conditions of a constant temperature at 303 K as well as vapor pressure of water at 2.5 kPa, which corresponds to the relative humidity of 60 %, using ethyl acetate as a model flavor in its vapor pressure range of 0 to 4.2 kPa and (b) to predict the amounts

of water and flavor migrated in a box of a tobacco product during storage.

EXPERIMENTAL

Flow-type Multi-component Adsorption System

The schematic drawing of a flow-type multi-component adsorption system is shown in Fig.1. Since the basic functions and operating methods of the system were the same as mentioned in the previous study⁽⁵⁾, only the additional devices concerning the supply and analysis of ethyl acetate vapor are described in this paper.

The vapor of ethyl acetate was supplied through bubblers which were immersed in another water bath, in the same arrangements as shown in Fig.1. The desired mixture of water and ethyl acetate was obtained at a location after valve (5) by mixing both saturated vapors. At the outlet of the adsorption cell, the concentration of ethyl acetate vapor was analyzed with the flame ionization detector (FID) of the gas chromatograph by operating a six-way cock and using a sampling tube.

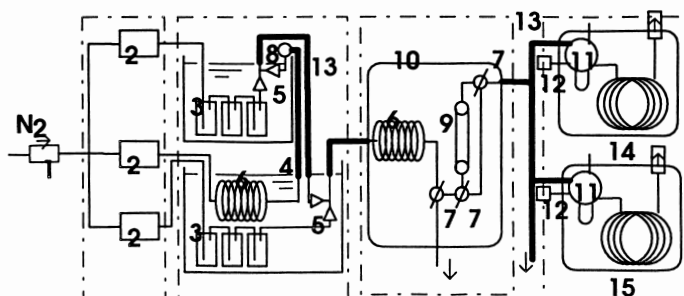
Materials

Fig.2 illustrates the materials contained in a box of a tobacco product, and the micropore volume (v_p) as well as the specific surface area (S) of activated carbon, which was obtained by the nitrogen adsorption isotherms, are indicated in Table 1.

Since the adsorption of flavor appeared to be affected by the flavor solubility into water as mentioned above, ethyl acetate, whose water solubility is 1ml/10ml-water at a temperature of 298 K⁽¹²⁾, was examined as a model for water-soluble volatile flavors because its physical properties such as the vapor-liquid equilibrium and solubility were well known.

Procedure

To obtain reproducible values for the adsorption isotherms, it was necessary to remove intrinsic volatile compounds and any adsorbed vapor. Therefore, the materials were put into the adsorption cell and dried under vacuum. These pretreatment conditions were 353 K for 8



1. dryer 2. flow meter controller 3. bubbler 4. water bath
 5. valve 6. heat exchanger 7. three-way cock 8. valve
 9. adsorption cell 10. air bath 11. six-way cock
 12. flow controller 13. heater 14. gas chromatograph(FID)
 15. gas chromatograph(TCD)

FIGURE 1 Flow-type multi-component adsorption system

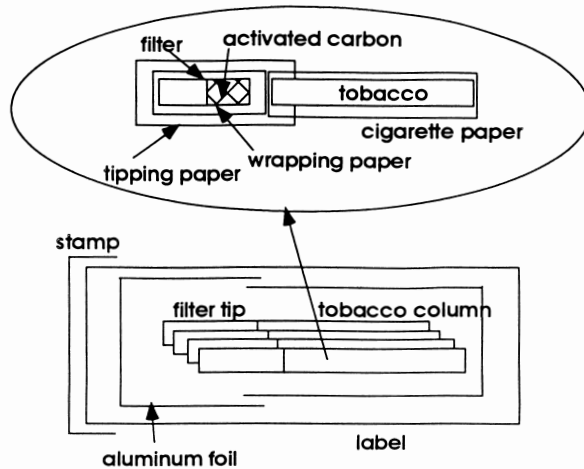


FIGURE 2 The materials contained in a box of a tobacco product or cigarettes

Table 1 Physical properties of activated carbon

Activated carbon	Micropore volume $\times 10^3$	Specific surface area $\times 10^{-3}$
	[m ³ /kg]	[m ² /kg]
Coconut	0.49	1255
Oil palm	0.39	1039
Coconut in filter	0.22	529

hours for tobacco, 373 K for 8 hours for paper as well as filter, and 473 K for 3 hours for activated carbon under the pressure range of 10^{-1} Pa⁽⁶⁾. Then the solid content of the material to be tested was determined by weighing the cell after drying.

Following the pretreatment, the cell was attached to the adsorption system and then the operation of adsorption was started. Dehumidified nitrogen was passed through the bubblers of water and then injected into the cell until equilibrium was attained at a relative humidity of 60 %. Then, the desired mixture of water and ethyl acetate vapor was injected into the cell, maintaining a constant temperature of the cell at 303 K. The times required for the materials to attain binary equilibria with the flowing gas were less than 4 minutes for tobacco and paper, 30 minutes for filter, and 30 minutes (90 minutes at $p_f = 0.16$ kPa) for activated carbon. In order to obtain reliable data for the adsorption isotherms, we continued to flow the mixture through the cell for over 2 hours after the agreement between the concentration of the inlet and outlet had been confirmed by the gas chromatograph.

After finishing adsorption, the cell was attached to the desorption equipment as shown in Fig.3. The apparatus (a) was used for all materials except activated carbon in which the absorbed agents were desorbed by heating the cell at 403 K for 1 hour using the dehumidified helium gas as a carrier. For activated carbon, the absorbed agents were desorbed by the vacuum heating method at a constant temperature of 473 K for 3 hours, using apparatus (b). Then they were collected with a liquid nitrogen trap in both sets of equipment. The trapped liquid was

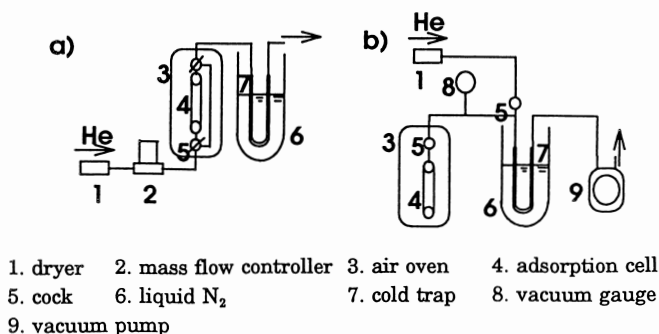


FIGURE 3 Two types of desorption equipments

diluted with ethanol to measure each amount of water or ethyl acetate with the thermal conductivity detector (TCD) or the flame ionization detector (FID) of the gas chromatograph, respectively. The preliminary tests confirmed that these desorption conditions were adequate to ensure that the adsorbed water and ethyl acetate could be measured accurately.

The adsorbed amounts of the pure component were obtained based on the weighing method of the cell as mentioned in the previous study⁽⁵⁾.

Adsorption in liquid phase

In the lower range of vapor pressure of ethyl acetate, the adsorption for the activated carbon could appear to be caused not by capillary condensation but rather by adsorption on the surface or onto the micropores. So, if no effect of the adsorbed water on the adsorption ethyl acetate for the activated carbon can be assumed, the adsorption isotherm in the vapor phase can be considered to coincide with that in the liquid phase or solution, in the lower range of vapor pressure of ethyl acetate. Therefore, the adsorption equilibrium in the liquid phase was measured using the following procedures⁽⁷⁾; The activated carbon was immersed in the aqueous solution of ethyl acetate in a flask. Then it was shaken for over 7 days in a water bath with a constant water temperature of 303 K. The initial and final concentrations of ethyl acetate in the solution were measured and the amount of adsorbed ethyl acetate was calculated.

RESULTS AND DISCUSSION

Tobacco

The binary adsorption isotherms for bright yellow and Burley tobaccos are shown in Fig.4. In the figure, the amounts of adsorbed water (q_w) and ethyl acetate (q_f) were plotted against the various vapor pressures of ethyl acetate (p_f). The results showed that q_w was nearly equal to the amount of pure water-vapor adsorbed at $p_w = 2.5$ kPa within a range of our measurements indicating the tendency to be almost independent of p_f , while q_f increased proportionally with increasing p_f as shown in a linear regression curve expressed as follows;

$$q_f = k \times p_f \quad (1)$$

where k is an empirical constant and its obtained values are presented in Table 2.

To investigate the mechanism of the binary adsorption characteristics obtained, the mole fraction of ethyl acetate in the vapor phase (y_f) was plotted against that in the liquid phase (x_f), comparing with a curve of the vapor-liquid equilibrium in the water and ethyl acetate system, as shown in Fig.5. The curve, which was reported by Komatsu et al.⁽⁴⁾, represents a vapor-liquid equilibrium relationship in a temperature range from 305 to 314 K under a constant total pressure of 2.0×10^4 Pa. Although the differences in absolute values existed between the curve and plots, each relationship qualitatively demonstrated almost the same behavior. As shown in Fig.4 there was a difference in the values of q_w between bright yellow and Burley tobaccos, while the values of q_f for them were in good agreement, as shown in Fig.4. These results lead to the conclusion that the mechanism of binary adsorption for tobacco is essentially explained in terms of the vapor-liquid equilibrium, and the water in the first or few adsorbed layers of the surface does not contribute to the adsorbed amount of ethyl acetate. As this mechanism is easily expected for tobacco, the empirical constants k was almost proportional to q_w under the water-vapor pressure ranging from 2.1 to 3.0 kPa.

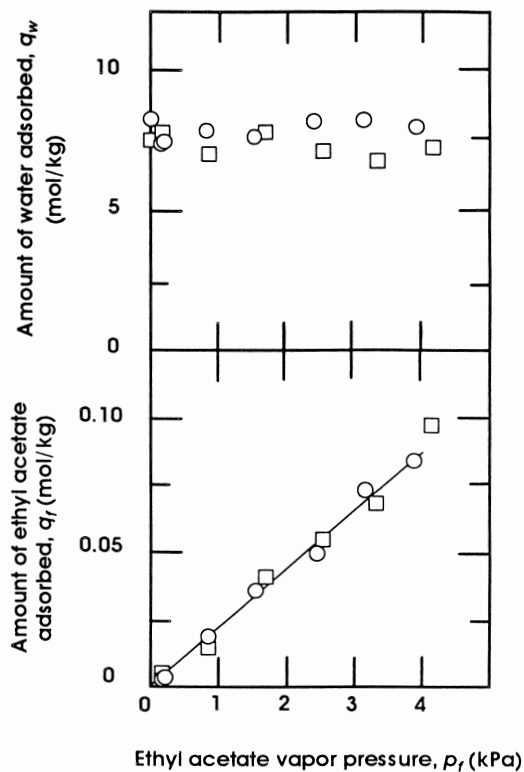


FIGURE 4 Equilibrium amounts of water and ethyl acetate adsorbed for tobacco (○, bright yellow; □, Burley)

Paper

The binary adsorption isotherms for the various papers are shown in Fig.6, in the same manner as in Fig.4. The isotherms obtained for various papers were found to be comparable with those for tobacco, indicating the same adsorption characteristics. The values of k obtained are also listed in Table 2, and the empirical equation of adsorption isotherm for the cigarette paper is presented as a solid line in Fig.6. Comparing between the binary adsorption isotherm of the tobacco and paper, the empirical constants k were proportional to q_w , as is expected in terms of the aforementioned mechanism of the binary adsorption.

Table 2 Empirical constants of equilibrium adsorption isotherms

Material	empirical constant	
Linear eq.	k	
	[mol/kg/kPa]	
Tobacco	ethyl acetate	water
bright yellow	0.022	
Burley	0.022	
Paper		
cigarette paper	0.011	
tipping paper	0.010	
wrapping paper	0.009	
aluminum foil	0.009	
label(soft pack)	0.010	
label(hard pack)	0.012	
stamp	0.009	
Filter		
tow	0.289	0.241
filter	0.285	0.268
DA eq.	$w_f^{\circ} \times 10^3$	E
	[m ³ /kg]	[kJ/mol]
Activated carbon		
coconut	0.43	14.2
oil palm	0.36	13.2
coconut in filter	0.26	12.4

Filter

The adsorption isotherms of pure components for the tow are shown in Fig.7. As mentioned in the previous study⁽⁵⁾, the tow or filter swelled as water was adsorbed. Thus, the amount of adsorbed water is considered to be generally much greater than any of the other adsorbates. However, the amount of adsorbed ethyl acetate was found to be of an equal order to that of water as shown in Fig.7. This means that the interaction between ethyl acetate and the tow is as much as

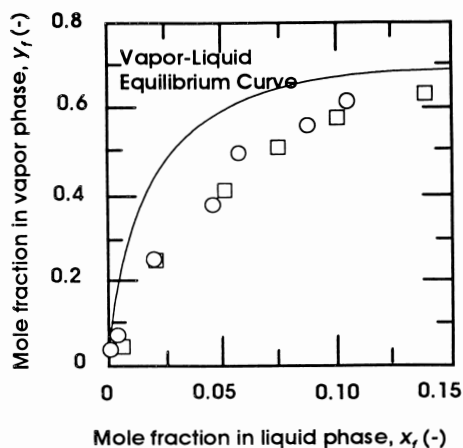


FIGURE 5 Relationship between mole fraction in liquid and vapor phase (○, bright yellow; □, Burley)

that between water and the tow. These characteristics of adsorption for the tow could be best interpreted in terms of ethyl acetate adsorbed on the hydrophobic sites which belong to the acetyl groups of the tow.

In Fig.8 the binary adsorption isotherms for the tow and filter are presented, comparing with the isotherm obtained for pure ethyl acetate, which is shown as a broken curve. Since the difference in the adsorption isotherms for both tow and filter did not appear definitely, it was revealed that triacetin, which was usually added as a plastic agent during the molding process of the filter, did not contribute to the binary adsorption for the filter. As the vapor pressure of ethyl acetate was increased, the amount of adsorbed water decreased but that of ethyl acetate increased proportionally. Then the linear regression curves for q_w within a p_f range below 3.2 kPa and q_f as a function of p_f were provided in Fig.8 and both values for their empirical constants were listed in Table 2.

These results suggest that the mechanism for these materials was different from that for tobacco as well as papers as mentioned previously. Decreasing in q_w is explained to be due to the partial desorption of water adsorbed on the hydrophobic sites of the material.

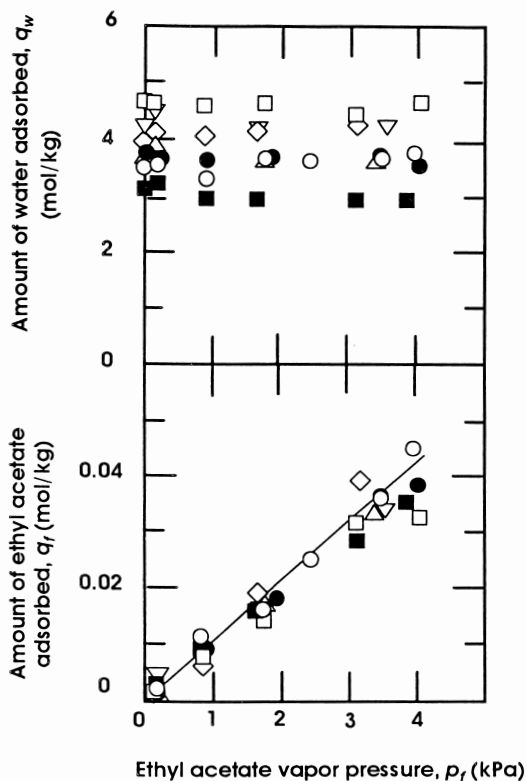


FIGURE 6 Equilibrium amounts of water and ethyl acetate adsorbed for papers

(○, cigarette paper; ●, tipping paper; □, wrapping paper;
 ■, aluminum foil; ◇, label(hard pack); △, label(soft pack);
 ▽, stamp)

Comparison between the pure and binary adsorption isotherms demonstrated that the amount of adsorbed ethyl acetate from binary vapor was always greater than that from pure ethyl acetate vapor. This phenomena was explained by considering the adsorbed water as an agent for the structural swelling of the material, leading to its larger surface area to adsorb a relatively greater flavor component from the binary vapor.

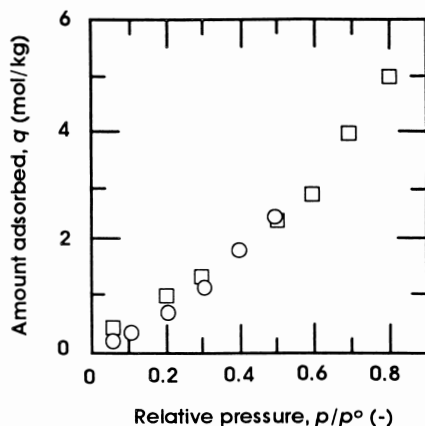


FIGURE 7 Equilibrium amounts of pure component adsorbed for tow (○, ethyl acetate; □, water)

Consequently, the phenomena of binary adsorption for both tow and filter is characterized by the increased effective surface area due to swell caused by adsorbed water and also the competitive adsorption among the components of the binary vapor on the hydrophobic or hydrophilic sites on the extended surface.

Activated Carbon

The binary adsorption isotherms for the activated carbons obtained from the coconut, oil palm and coconut contained in filter are shown in Fig.9. The data obtained from the adsorption experiments employing pure ethyl acetate vapor were also plotted in the figure. As p_f was increased, q_w approached a value of nearly zero, while q_f increased as a step function. It is generally known that if the vapor of an organic solvent such as acetone exists in the surface of the pore spaces of activated carbon, it is substituted for water adsorbed on the pores⁽¹⁰⁾. Ethyl acetate appeared to demonstrate the same behavior, and then it was adsorbed onto the micropores. Since no marked discrepancies in the plots of q_f were found between pure and binary adsorption, the effect of adsorbed water on the adsorption of ethyl acetate was confirmed to be as small as to be negligible.

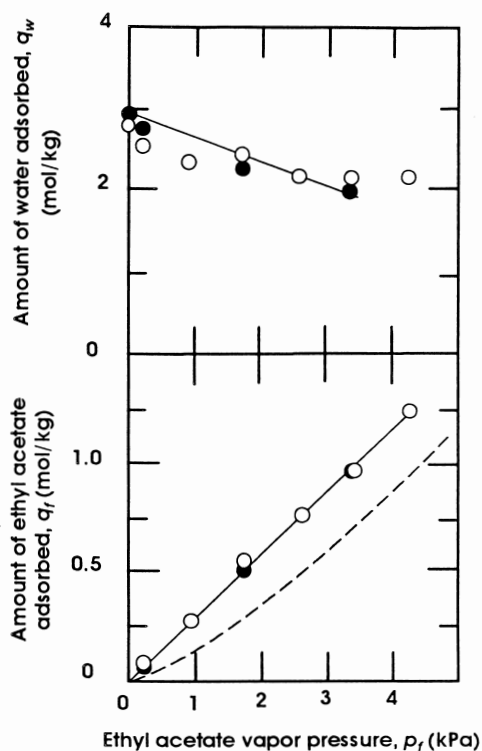


FIGURE 8 Equilibrium amounts of water and ethyl acetate adsorbed for filters (○, tow; ●, filter)

The adsorption isotherms in the liquid phase of the same binary system were also measured for these activated carbons, and the results obtained are shown in Fig.10, plotting the amounts of adsorbed ethyl acetate (q_f) against the mole fraction of it in the solution (x_f). The values of p_f were calculated from the vapor-liquid equilibrium relationship for the water and ethyl acetate system⁽⁴⁾, and for example, $x_f = 1.3 \times 10^{-4}$ is in equilibrium with $p_f = 0.16$ kPa in this system. Since the obtained values of q_f at $p_f = 0.16$ kPa for the vapor phase (shown in Fig.9) were consistent with that at $x_f = 1.3 \times 10^{-4}$ for the liquid phase (shown in

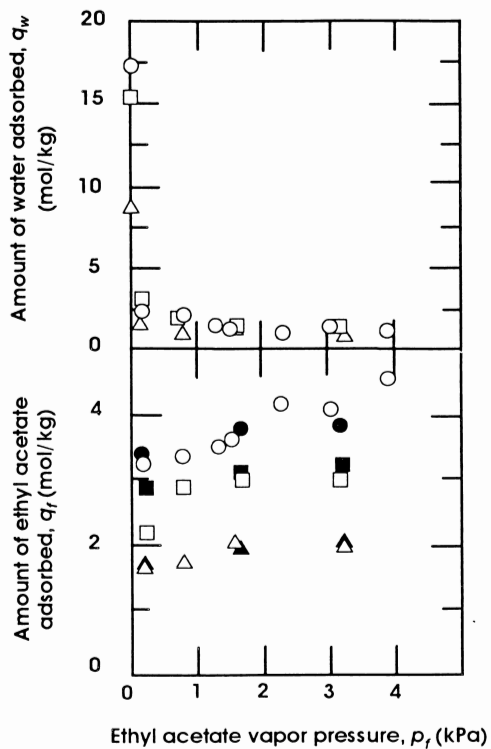


FIGURE 9 Equilibrium amounts of water and ethyl acetate adsorbed for activated carbons

(binary adsorption; ○, coconut; □, oil palm; △, coconut in filter;
pure adsorption; ●, coconut; ■, oil palm; ▲, coconut in filter)

Fig.10), the adsorption isotherm of ethyl acetate in the lower range of p_f could be measured easily by using the liquid phase or solution system.

The Dubinin-Astakhov (DA) equation, which is expressed as equation (2), is known to fit well for the adsorption data of organic solvents on activated carbon⁽²⁾⁽³⁾.

$$w_f = w_f^o \exp \left[- \left(\frac{A}{E} \right)^n \right] \quad (2)$$

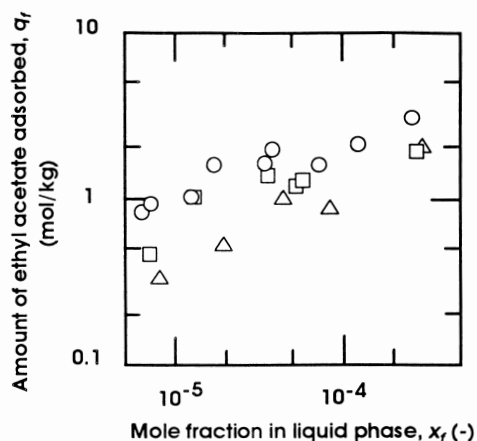


FIGURE 10 Equilibrium amounts of ethyl acetate adsorbed in liquid phase (○, coconut; □, oil palm; △, coconut in filter)

where w_f^o is the micropore volume and A is given as $A = RT \ln (p_f^o/p_f)$. The value of n is 2 for the organic solvent adsorption of activated carbon. w_f is given as $w_f = (q_f \times M) / \rho$. The experimental amounts of adsorption were plotted against the square of the adsorption potential (A^2) in Fig.11. The value of A in the liquid phase adsorption was determined from the vapor-liquid equilibrium relationship by calculating p_f from x_f . The DA equation was demonstrated to fit the adsorption data obtained as shown in Fig.11. The empirical constants for w_f^o or E in equation (2) are listed in Table 2. Since no marked differences in the values are found between w_f^o and v_p , the obtained DA equation was confirmed to provide verified values.

Since some of the micropores of activated carbon obtained from the filter were filled with triacetin which was added in the molding process of filter⁽¹⁰⁾, the value of q_f for it was half as much as that for coconut because of the effect of triacetin. It is well known that activated carbon exerts catalytic activities⁽⁹⁾. Because no other components of vapor or adsorbates could be detected except for water and ethyl acetate, each activated carbon at a temperature of 303 K did not exert any catalytic activity, such as hydrolysis of ethyl acetate.

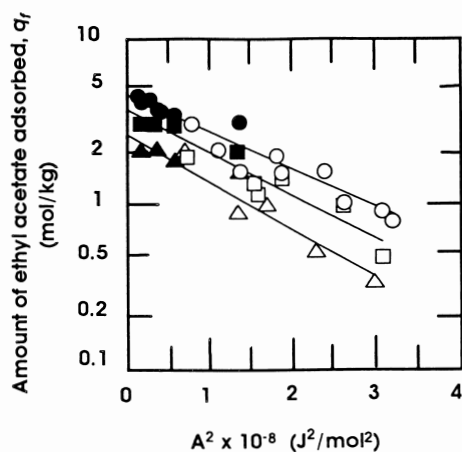


FIGURE 11 Dubinin plot of amounts adsorbed in liquid and vapor phase
 (liquid phase; ○, coconut; □, oil palm; △, coconut in filter;
 vapor phase; ●, coconut; ■, oil palm; ▲, coconut in filter)

Prediction of water and flavor migrations

The phenomena of water and flavor migrations were considered for each material during storage and marketing by utilizing the binary adsorption isotherms obtained.

Each material, which was stored under a condition of relative humidity at 60 %, is usually used in the manufacturing process and the application of volatile flavor to the tobacco is carried out under the same condition. So, the amount of water and flavor migrations for each material were predicted when each material was adjusted to the EMC at a constant relative humidity of 60 %, and then ethyl acetate was applied to the tobacco as a flavor. We assumed that (a) a box of a tobacco product contained tobacco columns of 25 mm in circumference, 70 mm in length and 700 mg/cig. in weight using equally mixed tobacco varieties of bright yellow and Burley, and a filter made from charcoal and cellulose acetate with a length of 10 mm and 15 mm, respectively, and (b) mass transfer through the packaging film was ignored. The materials were grouped into 4 categories based on their adsorption

characteristics obtained in this study; i.e. tobacco column, filter tip, pack and vapor.

In Fig.12, water migration among each category of the materials was represented as a function of the total amount of ethyl acetate, which applied to the tobacco in the flavoring process. The ordinate represents the increased and decreased amounts of water after the equilibrium in mass transfer was reached within a box of a tobacco product during its long term storage. The results showed that water migrated from the filter tip to the tobacco column depending on their selective characteristics on adsorption.

In Fig.13, the distribution of ethyl acetate as a model flavor among each category within a box was shown as a function of the total amount of ethyl acetate as mentioned above. The result indicated that the flavor component or ethyl acetate migrates from the tobacco column to the filter tip, and then most of it is accumulated inside the filter tip.

From these results the coupled water and ethyl acetate migration have been recognized to occur among the materials within a box as illustrated in Fig.14. Ethyl acetate migrates from the tobacco column to the filter tip, and spontaneously water moves backward. These migrations are undesirable because they cause the degradation of quality of the cigarette. For example, not only the loss of the flavor component from the tobacco column fails to conserve flavor to hold the desirable smoke odor and taste, but also the higher water content accumulated in the tobacco column exerts a great influence on combustion for smoking and the mechanical property for forming the shape of the cigarette. Therefore, the design of the product or cigarettes as well as the manufacturing process, and selection of materials should be determined under careful consideration regarding water and flavor migrations, which spontaneously proceed during storage and marketing.

CONCLUSION

Binary adsorption isotherms for the tobacco, papers, filters, and activated carbons were measured with a flow-type multi-component adsorption system under the constant conditions of temperature at 303 K and vapor pressure of water at 2.5 kPa in the vapor pressure range of ethyl acetate from 0 to 4.2 kPa. A linear equation was *applied to*

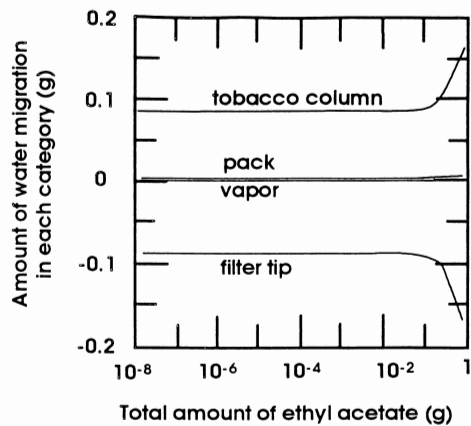


FIGURE 12 Calculated water configuration as a function of the total amount of ethyl acetate

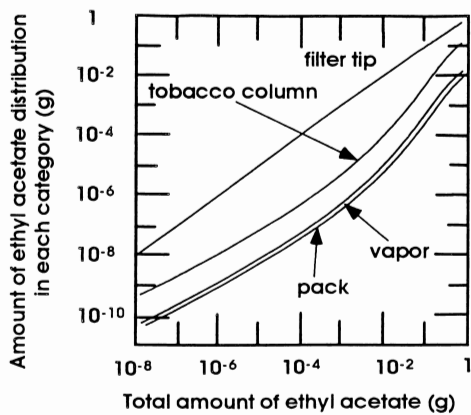


FIGURE 13 Calculated ethyl acetate distribution as a function of the total amount of ethyl acetate

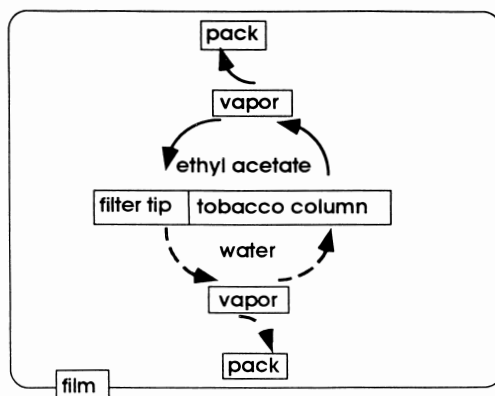


FIGURE 14 Schematic drawing of water and ethyl acetate migrations

express the binary adsorption isotherm for tobacco, papers and filters, while a Dubinin-Astakhov equation for activated carbons was applied. The binary adsorption was characterized into three groups, depending on the selectivity as well as the mechanism of adsorption. The binary adsorption characteristics suggested that; (1) for tobacco and papers, ethyl acetate was adsorbed by solution in the adsorbed water depending on the vapor-liquid equilibrium, (2) for filters, the competitive adsorption among water and ethyl acetate on the extended surface due to swelling caused by adsorbed water took place simultaneously, (3) for activated carbons, ethyl acetate was substituted for adsorbed water and adsorbed onto the micropores. Considering water and ethyl acetate migrations during storage and marketing by utilizing binary adsorption isotherms obtained, the coupled water and ethyl acetate migration have been recognized to occur among the materials within a box; ethyl acetate migrates from the tobacco column to the filter tip, and spontaneously water moves backward.

NOMENCLATURE

A	=free energy of adsorption	[J/mol]
E	=characteristic free energy of adsorption	[J/mol]

k	=constant in equation (1)	[mol/kg/kPa]
M	=molecular weight	[kg/mol]
n	=constant in equation (2)	[-]
p	=vapor pressure	[Pa]
p°	=saturated vapor pressure	[Pa]
q	=amount of adsorbed component	[mol/kg-dry material]
R	=gas constant	[J/K/mol]
s	=specific surface area	[m ² /kg-dry material]
T	=temperature	[K]
v_p	=micropore volume	[m ³ /kg]
w_f	=volume of adsorbed ethyl acetate	[m ³ /kg]
w_f°	=constant in equation (1)(=micropore volume)	[m ³ /kg]
x	=mole fraction in liquid phase	[-]
y	=mole fraction in vapor phase	[-]
ρ	=density	[kg/m ³]
<Subscripts>		
f	=ethyl acetate	
w	=water	

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