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Influence of Temperature on Membrane Permeability during Pervaporative Aroma Recovery

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ABSTRACT

The influence of operating temperature on membrane permeability was studied and compared with the effect of temperature on the driving force for permeation. A hydrophobic polyoctylmethyl siloxane membrane was used. For the feed mixture, an aqueous solution of aroma compounds containing four alcohols, one aldehyde, and five esters, all of which are important contributors to apple juice flavor, was used. Temperature had a strong effect on mass transfer and selectivity, both of which increased with increasing temperature. However, the selectivity for a component with a high activation energy for permeation increased more with temperature than did a component with a low activation energy for permeation. This caused a variation in the aroma composition of the permeate. The study showed that it is possible to estimate the activation energy for permeation of aroma compounds, and thus the influence of temperature on the internal mass transfer, through their hydrophobicity, size, and a complementary comparison of the activation energies for permeation for some other permeants of the same chemical group.

Key Words. Pervaporation; Aroma recovery; Permeability; Activation energy; Hydrophobic membranes

INTRODUCTION

Pervaporation is a membrane technique used for the separation of liquid mixtures by means of partial vaporization across a permselective membrane. The permeate is then obtained as a liquid by condensation. The driving force

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for permeation is established by maintaining a difference in partial pressure of the permeants across the membrane. This is accomplished in vacuum pervaporation by lowering the total pressure on the downstream side of the membrane. The mass transfer across the membrane can be described according to a solution–diffusion model (1) and can be divided into three consecutive steps: selective sorption of the liquid permeant into the membrane, selective diffusion through the membrane, and desorption into a vapor phase (2). External mass transfer must also be considered to evaluate the overall performance of the process. In several studies (3–7) it has been found that concentration polarization in the feed boundary layer may significantly affect the overall mass transfer. Due to very low downstream pressure, i.e., very low permeate concentrations, the effect of external mass limitation on the permeate side of the membrane is assumed to be negligible.

Some applications of pervaporation currently being developed involve the extraction of volatile hydrophobic molecules from dilute aqueous solutions; for example, the recovery of aroma compounds from fruit juices (8) or fermentation broths (9), the removal of inhibitors and/or the extraction of products from fermentation broths (10), and the removal of unpleasant odors from wastewater (4). In such applications, hydrophobic membranes are used in order to achieve high selectivity toward the hydrophobic molecules. Earlier work on pervaporative aroma recovery has shown that it is possible to obtain membrane selectivities in the 100–1000 range (8).

For optimization purposes it is necessary to study the influence of various process conditions on the performance of the process. The hydrodynamic conditions on the feed side of the membrane could be improved by the appropriate choice of module geometry and feed flow velocity (11). Increased flow velocity reduces the effect of concentration polarization in the feed boundary layer. Naturally, the downstream pressure acts on the driving force. The operating temperature influences the mass transfer in several ways. The external mass transfer is dependent on the viscosity of the feed and the diffusivities of the components in the mixture, both of which vary with temperature. The sorption rate of permeants onto the membrane and the diffusivities of the permeants inside the membrane material are also influenced by temperature. As the equilibrium vapor pressure of the permeants also varies with temperature, the driving force of the process is influenced by the temperature. All of these process parameters may affect the overall selectivities and the overall partial fluxes of the permeants considerably.

The aim of this study was to evaluate the influence of operating temperature on selectivities and partial fluxes during pervaporative aroma recovery from a model solution of apple juice aroma compounds. The behavior of 10 different aroma compounds was studied in order to find a way of predicting the variation in the selectivities and partial fluxes of the different permeants and the aroma profile of the permeate with temperature. Representatives from the three most important groups of aroma compounds present in apple juice, i.e., esters, aldehydes, and alcohols, were selected for the model solution (8). These all contribute significantly to the flavor of apple juice. The components were also chosen such that their hydrophobicities and molecular sizes could be related to their permeation behavior.

THEORY

The flux of component i, J_i, varies linearly with the gradient in partial pressure according to

$$J_i = \frac{P_i}{l}(p_{f,i} - p_{p,i}) \tag{1}$$

where $p_{f,i}$ and $p_{p,i}$ are the partial pressures of component i in the feed mixture and the vapor permeate, respectively; l is the thickness of the active layer of the membrane; and P_i is the permeability coefficient. According to Raoult's law, the partial pressure of component i in the feed is

$$p_{f,i} = \gamma_i X_{f,i} p_{0,i} \tag{2}$$

where γ_i is the activity coefficient, $X_{f,i}$ is the mole fraction in the feed, and $p_{0,i}$ is the equilibrium vapor pressure of component i. According to Dalton's law, the partial pressure of a component in the permeate can be expressed as

$$p_{p,i} = X_{p,i} p_p \tag{3}$$

where $X_{p,i}$ is the mole fraction of the component in the permeate and p_p is the permeate pressure. Due to a very low total permeate pressure, the partial pressure of the permeate is very small in comparison with the partial pressure of the feed and can be neglected. The flux can thus be assumed to vary linearly with the equilibrium vapor pressure of the pure component:

$$J_i = \frac{P_i}{l}\gamma_i X_{f,i} \mathrm{p}_{0,i} \tag{4}$$

As the partial flux is dependent on both the sorption to and diffusion through the membrane, the permeability coefficient is equal to the product of the solubility coefficient, S_i, and the diffusion coefficient, D_i, for component i (12, 13):

$$P_i = S_i D_i \tag{5}$$

The absorption step can be considered as a mixing process between the liquid and the polymer of which the membrane consists. The mixing of liquids and polymers is often a complex process due to interactions between the components, which result in a nonlinear sorption isotherm for the liquid. However, in the case of absorption of dilute organic–water mixtures to hydrophobic membranes, these interactions are often small, resulting in a linear sorption isotherm (14–16).

The diffusion coefficient of a permeant in a polymer is generally concentration-dependent and is affected by other components in the membrane. In the case of pervaporative aroma recovery, the concentrations of the organic permeants in the polymer will be very low, causing only a slight swelling of the membrane, and the transport properties of the permeants through the membrane will not vary significantly with their concentrations (17).

The temperature dependence of the solubility and the diffusion coefficients can normally be described by exponential relationships (13, 18):

$$S_i = S_{0,i} \exp(-\Delta H_{S_i}/RT) \tag{6}$$

$$D_i = D_{0,i} \exp(-E_{D_i}/RT) \tag{7}$$

where the subscript 0 denotes the property at a reference state; R and T are the gas constant and the temperature, respectively; ΔH_{S_i} is the enthalpy of dissolution; and E_{D_i} is the activation energy of diffusion. The enthalpy of dissolution is usually negative due to exothermic sorption processes (13). When Eqs. (6) and (7) are combined, the following relation is obtained:

$$P_i = P_{0,i} \exp(-E_{P_i}/RT) \tag{8}$$

where

$$P_{0,i} = S_{0,i} D_{0,i} \tag{9}$$

$$E_{P_i} = \Delta H_{S_i} + E_{D_i} \tag{10}$$

E_{P_i} is called the activation energy of permeation and describes the effect of temperature on the permeability of the membrane. It can be evaluated either through the slope of the ln $(J/\Delta p)$ vs $1/T$ plot (13, 18) or through the slope of the ln$(J/\Delta c)$ vs 1/T plot as the mass transfer driving force can be equivalently expressed as either the partial pressure gradient or the concentration gradient (1). The apparent activation energy, E_J, which is obtained through the slope of the ln J vs $1/T$ plot, is a compound parameter describing the overall temperature dependence of the permeation flux and thus includes the temperature dependence of the driving force (18). In the literature, E_J has been reported to be in the 20–80 kJ/mol range (19).

The selectivity of a membrane for a certain permeant often deviates from the apparent selectivity of the pervaporation process due to concentration polarization in the feed boundary layer. Due to favorable hydrodynamic conditions in terms of high Reynolds numbers, i.e., 22,000, the effect of concentration polarization was limited in this study and the apparent selectivity was close to the real selectivity of the membrane. The selectivity of the membrane is obtained from the intrinsic enrichment factor. The latter is defined as

$$\beta_{\mathrm{int},i} = X_{\mathrm{p},i}/X_{\mathrm{fm},i} \tag{11}$$

where $\beta_{\mathrm{int},i}$ is the intrinsic enrichment factor and $X_{\mathrm{p},i}$ and $X_{\mathrm{fm},i}$ are the permeate concentration of the component and the feed concentration of the component near the membrane surface, respectively.

MATERIALS AND METHODS

Feed Solution

A previously developed model solution of apple juice aromas was used as the feed solution (8). Aroma compounds in apple juice made of Spanish Granny Smith's apples were identified by gas chromatography (GC) and by gas chromatography together with mass spectroscopy (GC-MS). Ten of the identified compounds were selected for inclusion in a model solution of apple juice aromas. Each aroma compound was used at a concentration of 10 ppm (w/w), Table 1. Demineralized and distilled Milli-Q water, with a resistance greater than 18 MΩcm, was used as the solvent. The aroma compounds used to prepare the solution had a purity of about 99%.

Pervaporation Membranes

The membrane used was a POMS-PEI membrane, a polyoctylmethyl siloxane membrane supplied by GKSS Forschungzentrum, Geesthacht, Germany.

Pervaporation Apparatus

The experimental setup is shown in Fig. 1. A pervaporation module (see Fig. 2) with a membrane area of 150 cm^2 was used. It consists of two parts. In the first part, which has a length of 80 hydraulic diameters, the velocity profile is developed. The second part contains the membrane. The flow channel has a width of 60 mm, a height of 1.5 mm, and a hydraulic diameter of 2.93 mm. The retentate was recirculated to the temperature-controlled feed vessel (13 L). The permeate was collected in cold-traps by condensation, either with liquid nitrogen at −196°C or with dry ice at −56°C. Vacuum was achieved by a vacuum pump, which also separated inert gases from the permeate.

Experimental Procedures

The membrane was conditioned for 12–16 hours at a feed temperature of 20°C and a feed flow velocity of 3.6 m/s, with either Milli-Q water or the model solution used in the previous experiment, before each new experiment.

TABLE 1
Some Properties of the Aroma Compounds Used in the Model Solution and Water, Antoine's Constants and the Temperature Interval in Which They Are Valid, Aroma Threshold Values (ATV), Liquid Molar Volumes (V_m), Activity Coefficients in Water at Infinite Dilution (γ_w^∞), and Experimentally Determined Activation Energies for Permeation (E_P)

Component	Antoine's Constants	ΔT (°C)	ATV (ppm)	V_m (cm^3/mol)	γ_W^∞	E_P (kJ/mol)
Isobutanol	$A = 8.53516$(22)					
	$B = 1950.94$	−9–118	8–20(25)	102	56	50.1
	$C = 237.147$					
n-Butanol	$A = 7.60007$(23)					
	$B = 1439.57$	23–118	0.8–2(25)	104	56	54.1
	$C = 187.473$					
Isoamyl alcohol	$A = 7.82654$(23)					
	$B = 1616.21$	10–131	0.8–4(25)	124	150	57.6
	$C = 196.198$					
n-Hexanol	$A = 7.90589$(22)					
	$B = 1819.51$	24–157	0.9–1.9(25)	148	430	71.7
	$C = 205.086$					
trans-2-Hexenal	$A = 7.75757$(20)					
	$B = 2044.09$	—	0.017–0.085(26)	140	400	57.7
	$C = 273.15$					
Ethyl acetate	$A = 7.10179$(22)					
	$B = 1244.95$	16–76	9–45(25)	107	150	48.2
	$C = 217.881$					
Ethyl butanoate	$A = 7.20697$(23)					
	$B = 1509.44$	−18–121	0.008–0.03(25)	151	1,900	57.7
	$C = 227.866$					
Ethyl-2-methyl	$A = 7.35712$(23)					
butanoate	$B = 1536.99$	−24–110	0.000009–0.003(25)	171	5,600	60.0
	$C = 233.246$					
Isoamyl acetate	$A = 7.95557$(23)					
	$B = 1932.04$	41–95	0.009–0.04(25)	171	3,800	63.2
	$C = 244.452$					
Hexyl acetate	$A = 8.728$(24)					
	$B = 2558.1$	25–100	0.004–0.009(25)	296	11,000	74.1
	$C = 273.15$					
Water	$A = 8.07131$(22)					
	$B = 1730.63$		—	18.7	—	48.07
	$C = 233.426$					

During conditioning, dry ice was used for condensation, but during experiments liquid nitrogen was used. The permeate pressure was less than 2 mbar during both conditioning and experiments. During experiments the feed flow velocity was 7.4 m/s. This feed velocity corresponds to a Reynolds number of 22,000, and thus the flow was turbulent and the influence of concentration polarization on the feed side of the membrane was low. The feed temperature was varied in the 278–298 K range with an interval of 5 K. Three hours after

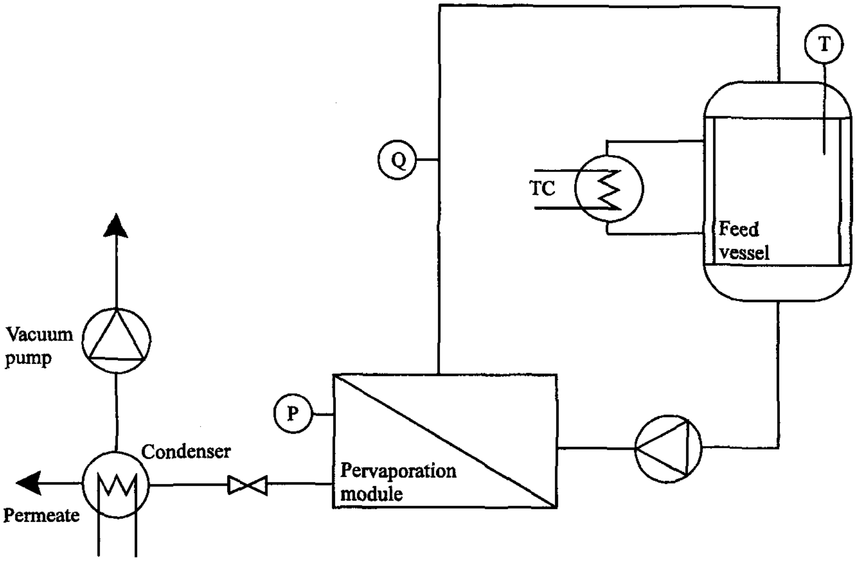

FIG. 1 Experimental setup of the pervaporation apparatus.

starting the pervaporation process using the model solution, the feed temperature was stable and the mass transfer equilibrium was deemed to have been established. Every hour the cold trap was exchanged and the permeate was thawed and poured back into the feed tank to limit the loss of aroma com-

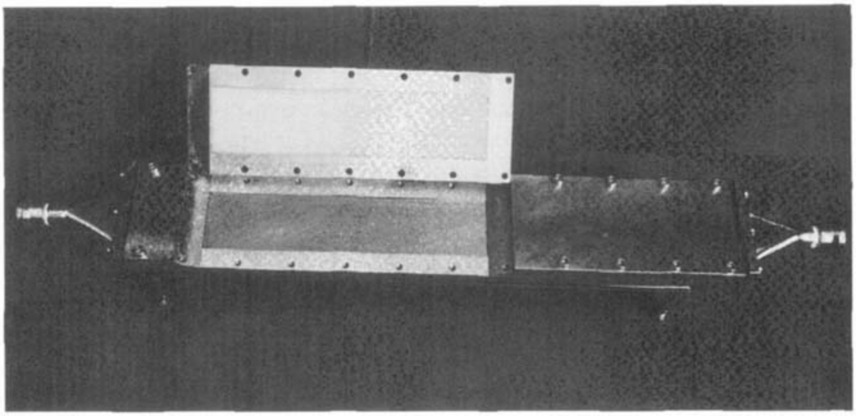

FIG. 2 The pervaporation module.

pounds from the tank. During the fourth hour the permeate was collected and samples from the feed tank were taken for analysis. Three experiments were performed at each temperature studied.

Analysis

The total flux was determined gravimetically, with an experimental error of 1–2%. The concentrations of aroma compounds in both the feed and the permeate were analyzed with a Varian Vista 6000 gas chromatograph (Varian Associates, Sunnyvale, CA, USA). The gas chromatograph was equipped with a fused silica capillary GC column (NB-351, 25 m, 0.32 mm, Nordion Instruments Oy Ltd, Helsinki, Finland). The temperature was programmed from 55 to 93°C at a rate of 4°C/min and then from 93 to 110°C at a rate of 30°C/min, with an initial hold of 2 minutes and a final hold of 3 minutes. The injector and detector were set to 180 and 190°C, respectively. The carrier gas was nitrogen, at a flow rate of 0.85 mL/min, and the sample was split 1:125 in the injector. 1-Pentanol was used as the internal standard. Each concentration determination was based on three or four different injections. The values of aroma concentrations varied by 5–10%.

PROPERTIES OF THE AROMA COMPOUNDS

Some properties of the aroma compounds and water are presented in Table 1. The activity coefficients at infinite dilution in water at 20°C and 1 atm were estimated using a UNIFAC method (20). The activity coefficient at infinite dilution in water can be considered to be a measure of the hydrophobicity of the molecule (21). Linear relationships between the hydrophobicity of molecules of the same chemical group, in this case esters, and their solubility coefficients for sorption to silicone rubber have been reported in the literature (21). The activity coefficients of the permeants in the feed mixture affect the driving force for permeation according to Eq. 4. The activity coefficient depends on composition and temperature. Due to very low concentrations of the aroma compounds in the feed, the activity coefficients of the aroma compounds will not deviate significantly from the activity coefficient at infinite dilution in water, and the activity coefficient of water will not deviate significantly from unity. The temperature dependence of the activity coefficient is usually very small compared with the temperature dependence of the pure liquid vapor pressures. Therefore, unless there is a large change in temperature, it is possible to neglect the effect of temperature on the activity coefficient when calculating vapor–liquid equilibrium (20).

The liquid molar volumes were estimated according to the Tyn and Calus method (20). The size of a molecule is closely related to the diffusivity of that molecule. According to the Stokes–Einstein equation, which is based on hydrodynamic theory, the diffusivity of solute *i* in a dilute liquid solution *j* is

$$D_{ij} = RT/6\pi\eta_j r_i \tag{12}$$

where η_j is the viscosity of the solvent and r_i is the radius of the "spherical" solute. A widely used correlation for estimating the diffusivity coefficient in liquids based on the Stokes–Einstein equation is the Wilke–Chang method (20) in which the liquid molar volume is related to the diffusivity coefficient according to

$$D_{ij} \propto 1/V_i^{0.6} \tag{13}$$

The equilibrium vapor pressures at different temperatures were obtained through Antoine's constants from the literature for all the compounds used except for *trans*-2-hexenal. In this case, Antoine's constants were estimated through a method based on the Clausius–Clapeyron equation (20). Antoine's constants can be used to estimate the equilibrium vapor pressure according to

$$^{10}\log p_{0,i} = A - \frac{B}{t + C} \tag{14}$$

where $p_{0,i}$ is the equilibrium vapor pressure of the pure component *i* in mmHg and *t* is the temperature in degrees centigrade. The variation of the equilibrium vapor pressure with temperature affects the driving force of the process.

Aroma threshold values, ATV, for the aroma compounds studied were found in the literature and are presented in Table 1. The ATV is often defined as the lowest concentration in a water solution at which the aroma compound is perceptible. Aroma compounds such as esters and aldehydes generally have very low ATVs, typically at ppb levels. This indicates that, although they are present at very low concentrations, they make an important contribution to the total intensity of the aroma complex.

RESULTS AND DISCUSSION

Influence of Temperature on Permeability

The activation energy of permeation for a permeant, $E_{P,i}$, determines the influence of temperature on the permeability of the membrane. The activation energies of permeation for the aroma compounds were determined through the slope of the ln $(J/\Delta p)$ vs $1/T$ plot, and are presented in Table 1. The standard deviations of the results for the alcohols and *trans*-2-hexenal were 3–6%, while they were somewhat larger for the esters, ranging from 7 to 14%.

Isobutanol and butanol have similar activity coefficients, i.e., similar hydrophobicities, but isobutanol is a more compact molecule, reflected by its smaller molar volume. A small molecule generally has higher diffusivity than a large molecule. The activation energy of diffusion for isobutanol should thus be smaller than for butanol, resulting in a smaller activation energy of permeation according to Eq. (10). The activation energies of permeation for isobutanol and butanol obtained were found to be 50 and 54 kJ/mol respectively, which confirms this reasoning.

Ethyl-2-methyl butanoate and isoamyl acetate have similar molar volumes, but ethyl-2-methyl butanoate is a more hydrophobic molecule, reflected by its larger activity coefficient. In analogy with the previous reasoning, the enthalpy of dissolution of ethyl-2-methyl butanoate should be lower than for isoamyl acetate, resulting in a lower activation energy of permeation according to Eq. (10). This was also the result as evidenced by the activation energies of permeation for ethyl-2-methyl butanoate and isoamyl acetate which were found to be 60 and 63 kJ/mol, respectively.

When moving from butanol to isoamyl alcohol and to hexanol, both the hydrophobicity and the molar volume are increased, see Table 1. This indicates increasing solubility but decreasing diffusivity, causing a decrease in the enthalpy of dissolution but an increase in the activation energy of diffusion. Because the energy of permeation increased from 54 kJ/mol for butanol to 58 kJ/mol for isoamyl alcohol and to 72 kJ/mol for hexanol, the increase in the activation energy of diffusion must have been larger than the decrease in the enthalpy of dissolution, i.e., the effect of reduced diffusivity was greater than the effect of improved solubility on the activation energy of permeation.

When moving from ethyl acetate to ethyl butanoate to ethyl-2-methyl butanoate and to hexyl acetate, both the hydrophobicity and the molar volume increase, i.e., the solubility is expected to improve while the diffusivity is expected to decrease. As the energy of permeation increased from 48 kJ/mol for ethyl acetate, to 58 kJ/mol for ethyl butanoate, to 60 kJ/mol for ethyl-2-methyl butanoate, and to 74 kJ/mol for hexyl acetate, the increase in the activation energy of diffusion must have been larger than the decrease in the enthalpy of dissolution. In other words, the effect of reduced diffusivity was greater than the effect of improved solubility on the activation energy of permeation, which is in accordance with the observed behavior of the alcohols.

A comparison can also be made between the chemical groups. Hexanol and ethyl butanoate are both linear C-6 molecules, although hexanol is slightly smaller than ethyl butanoate. As ethyl butanoate is considerably more hydrophobic, its enthalpy of dissolution should be smaller than that of hexanol, resulting in a smaller activation energy of permeation. This was also the case; the activation energy of permeation for ethyl butanoate was 58 kJ/mol and for hexanol was 72 kJ/mol. The small difference in size between the two molecules could, however, affect the activation energy of permeation slightly in the opposite direction because the activation energy of diffusion for ethyl butanoate is expected to be larger than for hexanol, resulting in a higher activation energy of permeation. The large difference in activation energy of permeation might not be entirely explained by the difference in activity coefficients, but also by the nature of the chemical group. The sorption of esters seems to be more rapid than the sorption of alcohols. A study by Lamer et al. (21) showed that for linear molecules with eight carbon atoms and a similar hydrophobic constant, i.e., ethyl hexanoate and 1-octen-3-ol, the order of sorption is ester > alcohol, and these results support the results obtained in this study.

The aldehyde, *trans*-2-hexenal, is also a linear C-6 molecule. Its activity coefficient is close to the activity coefficient of hexanol, but the molar volume is smaller. The activation energy of permeation was 58 kJ/mol, which is much smaller than 72 kJ/mol for hexanol. Part of the explanation of this large difference is that the activation energy of diffusion was smaller for *trans*-2-hexenal due to its smaller size, but part of the explanation could also be that the enthalpy of dissolution is smaller for *trans*-2-hexenal than for hexanol due to faster sorption of aldehydes in comparison with alcohols.

These comparisons support the suggestion that it may be possible to predict the activation energy of permeation for a component from three parameters: the chemical group to which the component belongs, the activity coefficient at infinite dilution in water, and the liquid molar volume.

Comparison of the Influence of Temperature on Permeability and Driving Force

As expected, the partial fluxes of both aroma compounds and water varied with temperature, according to Arrhenius expressions, because both the permeability and the equilibrium vapor pressure are generally reported to exhibit responses of this kind when the temperature is varied.

The contribution to increased partial flux with increasing temperature from enhanced sorption/membrane diffusion behavior is compared with the corresponding contribution from increased driving force of permeation, due to increased equilibrium vapor pressure of the pure component, in Figs. 3 and 4. In Fig. 3 the partial flux increase of one representative from each group of aroma compounds (i.e., isobutanol, *trans*-2-hexenal, and ethyl butanoate) and water are plotted versus temperature. The relative partial flux increase due to increased driving force was obtained for each component from Antoine's constants and these are also plotted in Fig. 3. The difference between the two curves indicates the contribution from improved sorption/diffusion behavior to the partial flux increase. Similar behavior was observed for the other permeants studied. In Fig. 4 the relations of the partial fluxes obtained at 298 and 278 K respectively for all the permeants are presented. The contributions from improved sorption/diffusion, i.e., permeation, behavior, and increased driving force to the flux increase, are also shown. For three of the alcohols, i.e., isobu-

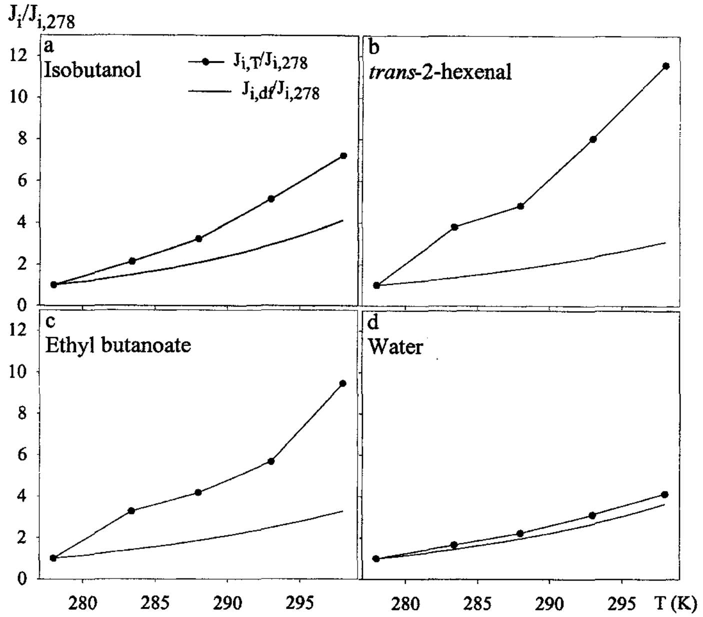

FIG. 3 The partial flux of four different permeants, one representative from each group of aroma compounds and water, i.e., isobutanol in (a), *trans*-2-hexenal in (b), ethyl butanoate in (c), and water in (d), related to the partial flux at the reference state (278 K). J_T/J_{278} is plotted versus the operating temperature. The relative partial flux increase due to increased driving force, $J_{df,T}/J_{df,278}$, for each component was obtained from Antoine's constants, and these are also plotted versus the operating temperature.

tanol, butanol, and isoamyl alcohol, the contributions from the two different phenomena were of the same order. For all the esters studied and for *trans*-2-hexenal and hexanol, the contribution from improved sorption/diffusion behavior to increased partial flux was considerably larger than the contribution from increased driving force. The opposite was found for water, i.e., the contribution from increased driving force dominated the partial flux increase when the temperature was increased, while improved permeability only had a small influence on the partial flux increase.

The Aroma Profile

Since the membrane exhibited different selectivities toward the aroma compounds, the composition of the permeate differed from that of the feed. In addition, the variation in selectivity, with regard to the aroma compounds, with temperature differed, which also affected the amounts of the various aroma compounds in the permeate. In Fig. 5 the intrinsic enrichment factors of the

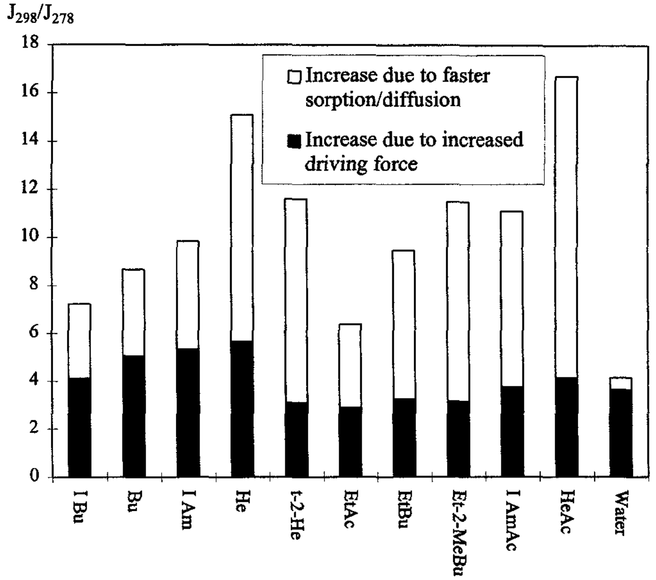

FIG. 4 The relation between the partial fluxes obtained at 298 and 278 K respectively for the permeants. The aroma compounds are abbreviated as follows: I Bu = isobutanol; Bu = butanol; I Am = isoamyl alcohol; He = hexanol; t-2-He = *trans*-2-hexenal; EtAc = ethyl acetate; EtBu = ethyl butanoate; Et-2-MeBu = ethyl-2-methyl butanoate; I AmAc = isoamyl acetate; HeAc = hexyl acetate.

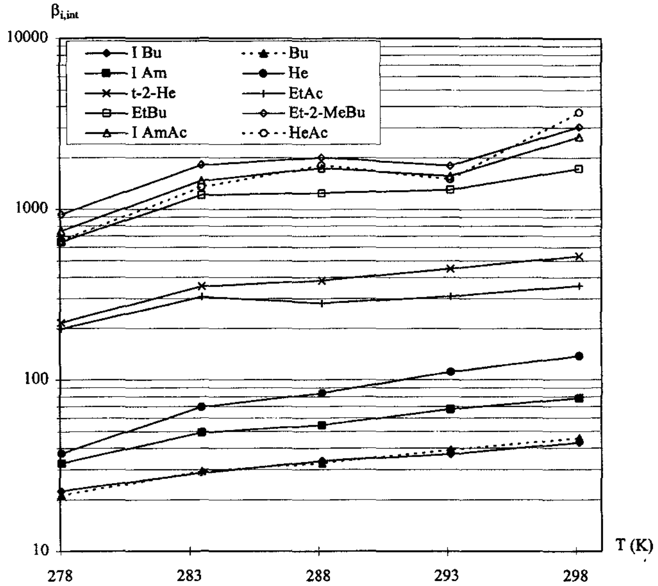

FIG. 5 The intrinsic enrichment factors of the aroma compounds, $\beta_{i,\text{ int}}$, plotted versus the operating temperature. The abbreviations for the aroma compounds are given in the Fig. 4 legend.

aroma compounds studied are plotted versus the temperature. The intrinsic enrichment factors of the alcohols, i.e., isobutanol, butanol, isoamyl alcohol, and hexanol, were high, i.e., in the 20 to 150 range. The intrinsic enrichment factors of *trans*-2-hexenal and ethyl acetate were higher, i.e., in the 200 to 500 range, and the intrinsic enrichment factors of the remaining esters, i.e., ethyl butanoate, ethyl-2-methyl butanoate, isoamyl acetate, and hexyl acetate, were the highest, i.e., in the 600 to 4000 range, which is in agreement with the results obtained in an earlier study (8). By comparing the amounts of aroma compounds in the permeate and the feed, it could be concluded that the content of esters and *trans*-2-hexenal is higher in the permeate than in the feed. The intrinsic enrichment factors increased considerably with temperature for all aroma compounds. When the temperature was increased from 278 to 298 K, the intrinsic enrichment factors increased by factors of 1.8 to 5.6, depending on the aroma compound. The increase was greatest for hexyl acetate, i.e., 5.6 times, while for ethyl-2-methyl butanoate, isoamyl acetate, and hexanol it was 3.2–3.8 times. The selectivities of the other aroma compounds studied increased by a factor 1.8 to 2.7. From a comparison of the activation energies of permeation for the different aroma compounds with their increased selectivities due to increased temperature, it is apparent that the compounds which require a large amount of energy for permeation are also the ones that gain the most in terms of improved membrane selectivity when the temperature is increased. The change in the composition of the permeate due to increased temperature might lead to a permeate with a slightly altered flavor. This effect was, however, small in comparison with the difference in flavor between the feed and the permeate. As the aim of pervaporative aroma recovery is to recover the main part of the aroma compounds from apple juice, the membrane area must be sufficiently large to recover most of the alcohols, which are limiting for the process due to their poorer mass transfer properties. This means that the aldehydes and the esters will be nearly fully recovered because they permeate faster than the alcohols.

CONCLUSIONS

The operating temperature had a significant effect on both mass transfer and selectivity during pervaporative aroma recovery. The effect of increased temperature on partial fluxes due to faster sorption/membrane diffusion was either equally important (for three of the alcohols studied) or considerably more important (for hexanol, *trans*-2-hexenal, and all the esters studied) than the corresponding effect due to the increase in the driving force for permeation. When considering the permeation of water, the increase in partial flux due to increased temperature was dominated by the effect of increased driving force for permeation. For all the aroma compounds studied, the intrinsic selectivities increased with increasing temperature, however, the intrinsic selectivity for a component with a high activation energy of permeation increased more with temperature than for a component with a low activation energy of permeation. This caused a variation in the aroma composition of the permeate with temperature. This effect was, however, small in comparison with the change in aroma composition between the feed and the permeate.

Thus, the study has shown that it could be possible to estimate the activation energy of permeation for aroma compounds, i.e., the influence of temperature on the internal mass transfer, through their hydrophobicity and size, using the activity coefficient in water at infinite dilution and liquid molar volume, respectively. A complementary comparison of the activation energies of permeation for some other permeants of the same chemical group is also needed. The sorption of esters seemed to be more rapid than the sorption of alcohols, yielding considerably lower activation energies of permeation when comparing permeants of comparable size.

These results imply that it may be possible to predict the influence of temperature on mass transfer and selectivity for various permeants.

SYMBOLS

A	Antoine constant (—)
B	Antoine constant (°C)
C	Antoine constant (°C)
D	diffusion coefficient (mol/m·s·Pa)
E_P	activation energy of permeation (kJ/mol)
E_D	activation energy of diffusion (kJ/mol)
ΔH_S	enthalpy of sorption (kJ/mol)
J	flux (mol/m^2·s)
P	permeability coefficient (mol/m·s·Pa)
R	gas constant (kJ/mol·K)
S	sorption coefficient (—)
T	temperature (K)
V	liquid molar volume (cm^3/mol)
X	mole fraction (—)
l	thickness of active layer (m)
p	pressure (Pa)
r	radius (m)
t	temperature (°C)

Greek Letters

β_{int}	intrinsic enrichment factor (—)
γ	activity coefficient (—)
η	viscosity (cP)

Subscripts

df	driving force
f	feed
i	component
j	component
m	near membrane surface
p	permeate
w	water
0	reference temperature

Superscripts

∞	infinite dilution

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