Recovery of Aroma Compounds from Dilute Model Blueberry Solution by Pervaporation

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ABSTRACT: Pervaporation (PV) is a membrane-separation process showing unique capability of separating target compound(s) from dilute systems. Experiments were performed on a bench-scale flat sheet PV unit with a model solution to evaluate separation factor of 6 constituent aroma compounds (1-hexanol, 1-heptanol, trans-2-hexenal, ethyl acetate, linalool, and d-limonene), representing some of typical flavoring ingredients from blueberry juice. The results showed that separation factor was in the range of 70 to 430, depending on molecule size and polarity property of the compounds. Except for 1-heptanol, all compounds showed no significant coupling effect in the mixture system. The effect of temperature was also examined for a given feed-flow rate.
Keywords: pervaporation, membrane, aroma compounds, blueberry, multicomponent diffusion

Introduction

Since the mid-1980s, there has been an increasing amount of research on pervaporation (PV) technology, ranging from membrane materials and module design to application and process model (Rautenbach and Albrecht 1985; Bell and others 1988; Lipski and Cote 1990; Karlsson and Trägårdh 1993; Michael 1995; Lipnizki and others 1999b; Vane and Alvarez 2002). The goal was to study and use the unique separation capability of PV in several industrial fields, including chemical engineering, environmental protection, pharmaceutical manufacturing, bioreactor fermentation, and the food industry (Aptel and others 1976; Nakao and others 1987; Karlsson and Trägårdh 1993; Domingues and others 1999; Shah and Bhattacharyya 1999; Bluemke and Schrader 2001; Peng and others 2003). PV can be defined as a process that separates the target compound(s) from a liquid feedstock based on the preferential partition of compounds into and consequent penetration through a nonporous membrane. Therefore, a characteristic of PV is a liquid-in and vapor-out process as regards to membrane matrix. The process is usually assisted by applying a vacuum (or sweeping gas) at the downstream side, thereby building a significant driving force under which those compound(s) that permeate into the membrane will desorb from the membrane underside in the form of vapor and will be condensed and collected in a cold trap afterward. Several reviews are available on basic PV principles and their applications (Karlsson and Trägårdh 1993; Semenova and others 1997; Lipnizki and others 1999a; Villaluenga and Mohammad 2000; Peng and others 2003). More than 60 PV units on an industrial scale were reported worldwide by 2002 (Jonquières and others 2002).

The main strength of PV is separating trace amount of compound(s) from liquid mixtures by using low temperatures and with high separation factors because of the presence of a perm-selective membrane barrier. Depending on the property of target compounds(s) to be separated, there are generally 2 types of PV membranes used, that is, hydrophobic membranes such as polydimethylsiloxane (PDMS), which show higher compatibility with hydrophobic compounds, and hydrophilic membranes, which have higher perm-selection for hydrophilic molecules. A schematic diagram for a PV process is shown in Figure 1. Two process parameters, flux (J) and selectivity (for example, separation factor [α]), are usually used for characterizing PV separation. Selectivity can be expressed in several ways. One common representation of selectivity, the separation factor, α, is analogous to the relative volatility of the component (i and j) of a binary liquid mixture. Sometimes, however, the enrichment factor (β_i), the ratio of concentration in permeate to concentration in feed is used as an indication of the separation selectivity for component i.

$$J_i = k_i \rho_i (C_i^L - C_i^v) \tag{1}$$

$$\alpha_{ij} = \frac{(C_i / C_j)^v}{(C_i / C_j)^L} \tag{2}$$

where k_i, ρ_i, C_i^L, and C_i^v are the overall mass transfer rate constant, density of feed, bulk liquid phase concentration (mass fraction), and bulk vapor phase concentration, respectively, for component i.

For the modern juice and fruit-processing industry, the importance of volatile aroma compounds cannot be overemphasized. Because most aroma compounds in fruit juice are prone to loss and damage during heat treatment, it is always desirable to find a way to reduce that loss and off-notes so that more desired flavor compounds will be present in the final food. By using PV, these compounds can be recovered at low temperature and incorporated into final juice products (Karlsson and Trägårdh 1996, 1997). Therefore, the formation of off-notes and the loss of flavor compounds because of evaporation could be minimized. Most studies on aroma compound(s) recovery were performed on a model solution representing a typical fruit juice flavoring profile. The reasons for using model solutions are 2-fold: (1) concentrations of most aroma compounds in fruit juices are very low and in some cases fall in the same order of magnitude as variations in concentration determination, and (2) the other constituent ingredients in juices might interact with permeating species and therefore distort the PV experi-

mental results and their presentations. Although there were studies by using raw juice or juice distillate as feed (Alvarez and others 2000; Pereira and others 2002; Shepherd and others 2002), these research were normally dedicated to specific applications, and therefore, their results were of limited significance in providing insights on mass transfer rate of each aroma compound of interest. The separation factors reported in literature (Karlsson and Trägårdh 1993, 1996, 1997; Lipnizki and others 1999b) for the typical aroma compounds in PV separation with PDMS membrane showed a general trend of ester > aldehyde > alcohol.

The primary objective of this research was to compare the separation factors of 6 selected aroma compounds and test the effect of feed rate on mass transfer coefficient in both binary and multicomponent environments. As shown in Table 1, the 6 compounds chosen represent 3 families of aroma compounds typical found in blueberry (Parliment and Kolor 1975; Horvat and others 1983). As noted in the literature (Honkanen and Hirvi 1982), there was no character impact compound in blueberry aroma, and the total amount of aroma compounds in blueberry is less than 2 ppm.

Materials and Methods

Materials

Chemical agents 1-hexanol, trans-2-hexenal, ethyl acetate, linalool, and d-limonene were purchased from Sigma Chemical Co (St. Louis, Mo., U.S.A.). 1-heptanol was obtained from Fluke (Milwaukee, Wis., U.S.A.). Methanol (99.9%, GC grade) was procured from Fisher Scientific (Suwanee, Ga., U.S.A.). Hydrophobic PDMS silicone rubber flat sheet membrane (0.0127 cm thick) was acquired from Specialty Manufacturing Inc. (Saginaw, Mich., U.S.A.).

Experiment setup and operating procedure

The experiment setup is shown in Figure 2. A laboratory-scale flat sheet membrane module with effective dimensions of the membrane holding cell of 2.4 cm × 16.4 cm, yielding an effective area of 39.36 cm^2, was used for all our experiments. Feed solutions first went through a heat exchanger to reach a steady temperature (30 °C unless otherwise stated) before entering the membrane module. The flow rate was controlled and indicated by a flow meter. Two cold traps were installed in parallel for condensing and collecting the vapor stream. The vacuum was kept between 2 to 3 torrs. Thermocouples were used for measuring temperatures of feed (before and after module) and vapor. A pressure sensor monitored pressure downstream. The permeate concentration kept on increasing at the start of operation. After about 3 h of initial operation, the permeate concentration reached a stable condition, and the steady-state separation was reached. The concentrations of feed and permeate samples were analyzed by GC. At the end of each
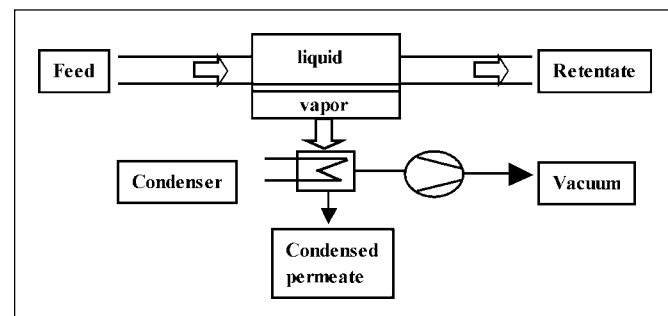
run, the cold trap was taken out, capped, and stabilized in a draft cabinet for 2 min to remove condensed moisture on the outside surface. The permeate was then weighted, diluted with methanol, and transferred to a 10-mL volumetric flask. For each set of operating parameters, 2 runs were performed to get replicate results.

In the binary PV experiments, each of the 6 aroma compounds was used in preparing a binary feed solution. The amount of most solutes added into water was controlled so that the final concentration would be around 20 ppm, whereas for d-limonene the saturated concentration was maintained in a feed tank. The precise concentration of feed at the beginning and the end of each run were determined by GC analysis. Because of the large feed tank volume (20 L), the variations of feed concentration during each run were negligible. In multicomponent mixture PV experiments, feed solutions were prepared in such a manner that it contained all 6 aroma compounds. For each tested feed solution, 3 feed flow rates were examined, corresponding to average velocities of 0.07, 0.14, and 0.21 m/s, respectively, over the upper-stream side of the membrane. The Reynolds numbers (Re = $d_h u \rho / \mu$, hydraulic diameter was 0.0037 m) at these velocities were 260, 520, and 780, respectively. In the experiments of evaluating the effect of temperature on PV performance, the flow rate was controlled so that the average velocity and Reynolds number were fixed at 0.07 m/s and 260, respectively.

GC analysis

GC Varian 3500 (Varian, Inc., Calif., U.S.A.) with flame ionization detector was used. The column was a J&W Scientific DB-1 (Agilent Technologies, Calif., U.S.A.) 60 m × 0.32 mm with 3-mm-thick film, detector 280 °C; injector temperature was held at 180 °C; carrier gas helium flow rate in the column was 2.5 mL/min; injection amount was 1 μL; split ratio was 12.7. The column was temperature programmed to start from 35 °C, held for 2 min, then increased to 170 °C at 10 °C/min, held for 2 min, then increased to 230 °C at 10 °C/min. Internal standard (fluorobenzene) retention time was 10.5 min. For each prepared sample, 3 injections were made to get triplicate GC results. The overall error from replication (including GC analysis) was within 10%.

Results and Discussion

Mass transfer coefficients in binary system

The experimental results of mass transfer coefficient k for binary
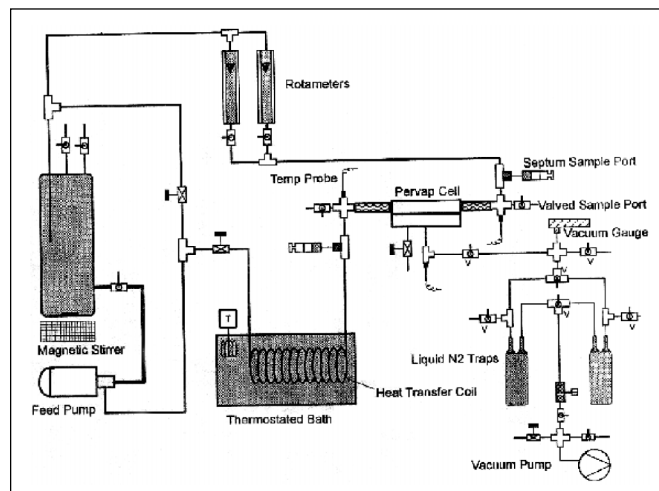
Figure 1—Schematic diagram for pervaporation system

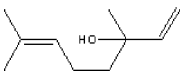
Figure 2—Experiment setup for pervaporation experiments
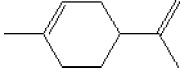
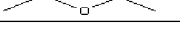systems are presented in Figure 3. The increase in velocity brought an obvious increase of k value for all tested aroma compounds. The k values were in the range of 0.2 to 1.1×10^{-5} m/s, with ethyl acetate and limonene being at the high end and low end of this range, respectively. Ethyl acetate has the smallest molecular size, and its polarity is lower than other aldehydes and alcohols, therefore making it permeate through membrane preferentially. d-Limonene, on the other hand, has relatively large and bulky molecular configuration, therefore hindering its passage through the membrane structure. The flux of limonene (0.02 to 0.06 g/m²h) and ethyl acetate (0.78 g/m²h, not shown in figures) showed a much larger difference than the difference between their k value because of the feed concentration difference, thus making the k values a better candidate for comparison of PV separation effect for different compounds. Because several operating parameters influence PV separation, such as module type, membrane matrix and thickness, feed condition, downside vacuum, and so forth, it is usually difficult to make comparison with the data from literature, even though the solute is the same. Therefore, some differences were expected. For example, literature reported enrichment factors of 78 for 1-hexanol, 337 for trans-2-hexenal, and 322 for ethyl acetate when PDMS was used (Karlsson and Trägårdh 1997), yet our experiments indicated that the separation factors were 192, 254, and 300 for these 3 compounds, as shown in Table 2.

In many PV processes, the available solute concentration at the feed-side membrane surface is much lower than that in the bulk solution because of the presence of concentration polarization. According to the resistance-in-series theory, the overall resistance in mass transfer can be expressed as $1/k$, and it consists of resistances from the boundary layer $1/k_{bl}$ and the membrane $1/k_m$ where k_{bl} and k_m are mass transfer coefficients within the liquid boundary layer and the membrane. When k_m is much larger than k_{bl}, which usually occurs in a laminar flow as in our experiments, the main resistance will come from the boundary layer. Thus, a decrease in the boundary layer resistance ($1/k_m$) by increasing feed velocity would have a large effect on the overall mass transfer coefficient, as was observed in Figure 3. The differences in overall mass transfer coefficient for the aroma compounds under same feed-flow rate can be explained by their difference of diffusivity in the feed-side stream and permeability in the membrane. Although k_{bl} can be estimated by empirical dimensionless correlations to get a reason-
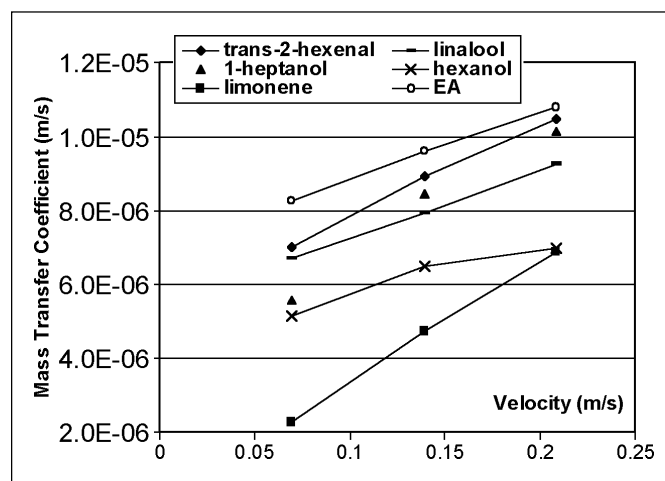
Table 1—Activation energy

Compound	Diffusivity in water (m²/s)	Activation energy (kJ/mol)
Water		34.7
Linalool	6.4×10^{-09}	21.6
d-Limonene	6.8×10^{-09}	11.1
1-Heptanol	7.3×10^{-09}	23.7
1-Hexanol	7.9×10^{-09}	32.5
Trans-2-hexenal	8.2×10^{-09}	19.0
Ethyl acetate	9.1×10^{-09}	16.2

Table 2—Separation factors for aroma compounds

Compound	Binary 30 °C	Mixture 30 °C	Mixture 40 °C	Mixture 50 °C
Linalool	249	231	237	167
d-Limonene	87	135	106	76
1-Heptanol	206	405	429	310
1-Hexanol	192	203	251	192
Trans-2-hexenal	254	267	268	162
Ethyl acetate	300	290	238	184

ably accurate value, the lack of information for calculating k_m precludes quantitative analysis for overall mass transfer coefficients for each aroma compound.

The diffusivity for the 6 compounds in water can be calculated by Wilke-Chang equation (Cussler 1997), as in Eq. 3.

$$D_j = 7.4 \times 10^{-8} \frac{(\psi_j M_j)^{1/2} T}{\mu V_i^{0.6}} \qquad (3)$$

where i represents the organic species and j signifies solvent (water in this case); D_j has units of cm²/s; V_i is molar volume (cm³/g-mol); M_i is molecular weight of species i; μ is viscosity of the solvent or solution (10^{-2} g/cm · s, that is, cP); T is absolute temperature (K); and the dimensionless constant ψ_j is 2.6 when water is the solvent. The diffusivity (in m²/s) for 6 compounds are shown in Table 1. The observed sequence of k value, however, was as follows: d-limonene < 1-hexanol < linalool ≅ 1-heptanol < trans-2-hexenal < ethyl acetate. So a possible explanation is that linalool has a relatively higher permeability in the membrane, which gave it a medium PV-separable rating despite its low diffusivity. The low k value for 1-hexanol, in a similar manner, can be attributed to its low permeability within the membrane matrix.

The 2 key coefficients k_{bl} and k_m for describing solute behaviors on the feed side and in the membrane matrix are the basis for a lot of research work in PV separations and modeling (Karlsson and Trägårdh 1993; Jiang and others 1997; Peng and others 2003). But there is one issue that cannot be addressed by this approach. Why did the mass transfer coefficients of some aroma compounds, such as 1-hexanol (which has relatively higher mass transfer coefficient at low Reynolds numbers), not respond to the velocity increase as drastically as some other compounds with low k values? According

Figure 3—Mass transfer coefficients as a function of average feed velocity for aroma compounds in binary solution at 30 °C

to the resistance-in-series theory, if a solute species has a small overall *k* value as a result of the resistance from the membrane (small permeability within the membrane), such as limonene in our case, then the effect of increase in feed-flow rate on increase in overall *k* value should be less significant compared with other species that show higher overall *k* values. This means the difference of *k* values between aroma compounds at a lower value of fixed velocity should be smaller than the difference at the higher velocity values, thus showing a divergent trend. The observed result was just the opposite, which showed a convergent trend. It is believed that the factor that needs to be taken into consideration is modeling the solubility of the solute in the membrane matrix as a function of solute concentration (Mulder 1991). Although the solute in the feed solution was present in low concentration, preferential permeation may raise the solute concentration in the membrane matrix to the extent that the assumption of constant solubility (and thus permeability) of the solute is no longer valid. Thus the solute-polymer interaction factor used in Flory-Huggins equation will be a variant and a different sorption would be expected (Chandak and others 1998).

In all experiments (including the following mixture experiments), water flux was found to be constant at about 98 g/m²h. This value was in agreement with the water flux when pure water was used as a feed solution. Therefore, there was no observable membrane swelling effect during the experiments at this feed concentration level.

Mass transfer coefficients in mixture

The outcome of the study of mass transfer coefficient *k* for mixture model solutions is shown in Figure 4. Although no remarkable changes were observed with regard to the absolute *k* values because of serious coupling effect for most of the aroma compounds, 1-heptanol showed a substantial increase (averaging 70% over the test range) in *k* value, rendering it the highest among all tested compounds. In the binary experiments, 1-heptanol showed high increase of the mass transfer coefficient with increased feed velocity, indicating its solubility in the membrane might have increased at higher feed concentration near the membrane, or the mass transfer resistance was relatively small compared with the resistance from the boundary layer. In the mixture systems, it is clear that the presence of other aroma compounds created an even more favorable environment for 1-heptanol's permeation through the

membrane. A more detailed analysis and quantification of this interaction effect are possible, but it would require more experiments to get the necessary parameters for modeling multicomponent performance in the membrane matrix.

There were some minor coupling effects for other compounds at the low and high ends of feed rates compared with the results from the binary experiments. At the low feed velocities, those compounds having lower mass transfer coefficients in binary solutions showed higher value in mixture. For example, limonene showed a nearly 100% increase of *k* from 2.1×10^{-6} to 3.95×10^{-6} m/s, indicating the positive coupling effect from the mixture. The small negative coupling effect for those compounds having higher mass transfer coefficients in binary solutions was obvious at the high velocities, as in the cases of ethyl acetate and trans-2-hexenal. Consequently, a somewhat parallel trend was observed between the lines describing the mass transfer coefficient for each compound as a function of velocity.

Effects of temperature

The increase in temperature affected the behavior of the compounds both in the feed solution (including diffusivity and viscosity) and in the membrane (permeability). Water flux usually will also increase under higher temperatures (Peng and others 2003). At 40 °C and 50 °C, the water fluxes were 155 and 230 g/m²h, respectively. Arrhenius-type relationships can be used in describing the effect of temperature by correlating flux as a function of temperature as follows:

$$J_i = J_0 * \exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

where J_i (g/m²h) represents the flux of species i; J_0 (g/m²h) is a constant; E_a (J/mol) is the activation energy; R (J/mol °K) is the universal gas constant; and T is the absolute temperature in Kelvin (K). When the value of E_a is high, the flux will be more sensitive to changes in temperature. The activation energy for the aroma compounds was calculated and is shown in Table 1. It can be seen that water was most responsive to temperature increase and showed the fastest increase of flux, and d-limonene had the least sensitivity to temperature change.

Because both water and aroma compounds showed flux increase under increased temperature, the separation factor will depend on the ratio of their increases. The separation factors for the 6 compounds at 30 °C to 50 °C are shown in Table 2 with the values for the binary systems shown as well. Owing to low concentrations in both feed and permeate, the separation factor illustrated in Eq. 2 is almost equal to the value of enrichment factor. For example, linalool was separated from 18 ppm binary solution at 30 °C and the permeate contained 0.45% of linalool, thus giving a separation factor of 249 and enrichment factor of 248. Ethyl acetate and limonene showed consistent decrease of separation factor, indicating that for a given feed solution, although higher temperature can bring more flux of the solute, its concentration in the permeate phase will decrease because of faster increase in water flux.

Conclusions

Six aroma compounds representing the blueberry aroma profile were separated from model solutions by PV with a PDMS membrane. Ethyl acetate showed the highest mass transfer coefficient, whereas limonene has the lowest value in the experiments of binary systems. In the mixture systems, a higher coupling effect was observed for 1-heptanol. When feed velocity was varied, the mass
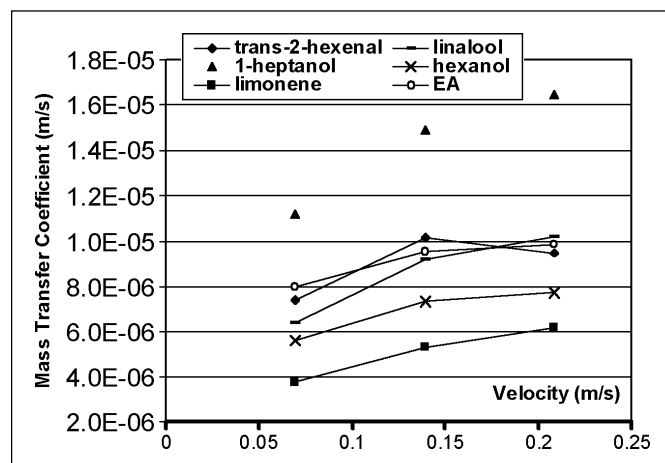
Figure 4—Mass transfer coefficients as a function of average feed velocity for aroma compounds in mixture at 30 °C

transfer coefficient of these compounds showed different patterns with k value varying from 0.2 to 1.6×10^{-5} m/s. The increase in separation effectiveness by increasing feed temperature was varied for tested aroma compounds. This effect, together with the interaction effect from the multicomponent system, will have a substantial influence in the composition of separated streams, which needs to be the focus of future research.

Nomenclature

C = concentration of the bulk fluid in mass traction

d = hydraulic diameter (m)

D = diffusivity (m^2/s)

k = overall mass transfer coefficient (m/s)

E_a = activation energy (kJ/mol)

J_i = flux (g/m^2h)

J_0 = constant in equation (4) flux (g/m^2h)

R = gas constant (8.31 J/mol K)

M = molecular weight

T = absolute temperature (K)

α_{ij} = separation factor for ingredient i relative to ingredient j, dimensionless

β = enrichment factor, dimensionless

μ = viscosity of solvent (g/m s)

V = molar volume $(cm^3/g\text{-}mol)$

ρ = density (g/mole)

Subscripts and superscripts

i = ingredient i

j = ingredient j

bl = boundary layer

m = membrane

v = vapor phase

L = liquid phase

Abbreviations

PV = pervaporation

PDMS = polydimethylsiloxane

VOCs = volatile organic compound

Re = Reynolds number

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