Concentration by pervaporation of representative brown crab volatile compounds from dilute model solution.

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In this work, the pervaporation technique is investigated in the separation of dilute solutions of volatile compounds from brown crab effluent in order to obtain a valuable food flavouring fraction. A systematic study of the pervaporation process has been carried out on dilute model solutions of some of the compounds identified in the brown crab effluent as typical volatile compounds. The membrane used in this work was a hydrophobic membrane with a selective layer of POMS (polyoctylmethyl siloxane). The effect of some operating variables, such as feed flow rate, feed concentration, feed temperature and permeate pressure was analyzed on the pervaporation performance of the membrane.

Keywords: volatile compounds, concentration, pervaporation, POMS membrane

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1. Introduction

Brown crabs are found in the Eastern Atlantic and are heavily exploited commercially being available throughout the year. The brown crab liquid effluent produced during boiling is believed to contain important amounts of volatile flavour components (Cha et al. 1993). This work is part of a wider study to consider the conversion of this by-product into valuable volatile concentrate. Concentrates of the volatile species have considerable commercial utility, especially in the food industry due to longer shelf life, reduced packaging and lower distribution and storage costs (She and Hwang, 2006). Additionally, organic removal from water at low concentrations involves an important environmental challenge.

Cha et al. (1993) studied the concentration of the liquid effluent produced during snow crab boiling by steam distillation. However, this technique involves high energy consumption as well as physical aroma losses (García et al. 2008). In this work, the pervaporation process has been considered to recover the volatile fraction from brown crab effluent. Pervaporation is a membrane process which has been developed rapidly in the last 20 years for aroma concentration (She and Hwang, 2006) since the addition of chemical solvents is avoided. Additionally moderate operating temperatures help to minimize degradation of aroma character.

Brown crab effluent was supplied by IDOKI SCF Technologies S.L. (Spain). The first step in this work was to determine the main volatile organic compounds present in the industrial effluent. More than 150 compounds were identified in the brown crab effluent. These included mainly aldehydes, ketones, alcohols, esters, aromatic compounds and sulphur and nitrogen-containing compounds. To study the ability of pervaporation process to recover the volatile fraction from the brown crab effluent seven of the identified compounds have been selected for a model aqueous solution of brown crab effluent: 1-octen-3-ol, 1-penten-3-ol, 3-methylbutanal, hexanal, benzaldehyde, 2,3-pentadione and ethyl acetate.

A systematic study of the pervaporation process of the dilute model solution was performed in order to analyze the influence of some operating variables on the pervaporation performance. The permeation flux and enrichment factor of the selected volatile compounds were analyzed at different operating conditions: feed flow rate, feed temperature, feed concentration and permeate pressure.

2. Theory.

On the basis on the solution/diffusion model the flux of component i through the membrane is proportional to the difference in partial vapor pressure at both sides of the membrane (Blume et al. 1990):

$$J_i = Q_{OV,i}\left(x_i \gamma_i p_i^s - y_i p_p\right) \tag{1}$$

where J_i is the partial permeation flux, Q_{OVi} the pressure-normalized permeation flux (permeance), x_i the mole fraction of component i in the feed, γ_i the activity coefficient and p_i^s the saturation vapor pressure at the temperature of the feed, y_i, the mole fraction in the permeate and p_p the permeate pressure. In case of pervaporation of dilute aqueous solutions activity coefficients at infinite dilution in water (γ_i^∞) are used as feed-side activity coefficients due to the very low concentrations of aroma compounds in the feed (Trifunovic and Trägardh, 2006). In this work, the activity coefficients at infinite dilution in water were estimated with the help of the software Aspen plus (2008) by using UNIQUAC equation when binary interaction parameters were available, otherwise the predictive method UNIFAC-Dortmund was used.

According to the resistance-in-series model, the two main mass transfer resistances that affect the pervaporation process are the liquid boundary layer resistance and the membrane resistance. At steady state the flux through the different mass transfer layers is equal:

$$J_i = Q_{ov,i}\left(x_i \gamma_i p_i^s - y_i p_p\right) = k_{bl,i}\rho(x_i - x_i^m) = Q_{m,i}\left(p_i^m - y_i p_p\right) \qquad (2)$$

where k_{bl} is the liquid boundary layer mass transfer coefficient, ρ the total mass volume concentration of the feed, x_i^m mol fraction of i at the membrane-fluid interface, $Q_{m,i}$ the pressure normalized permeation flux across the membrane and p_i^m the partial vapor pressure of i at the membrane-fluid interface. The rest of the symbols are the same as in Equation 1. The overall mass transfer coefficient in the steady state can be expressed as the sum of these two resistances:

$$\frac{1}{Q_{ov,i}} = \frac{\gamma_i p_i^s}{k_{b,l}\rho} + \frac{1}{Q_{m,i}} \qquad (3)$$

The term $\gamma_i p_i^s / \rho$ is the conversion factor from a concentration driving force to a partial vapour pressure driving force. The overall mass transfer coefficient $Q_{OV,i}$ of Eq. 1 can be obtained from experimental measurements of the permeate flux and feed concentration of the permeating component i. The liquid boundary layer mass transfer coefficient, k_{bL}, is related to the feed hydrodynamic conditions and it can be estimated from the Sherwood correlation in terms of Reynolds (Re) and Schmidt (Sc) numbers for a plate-and-frame module (Dotremont et al. 1994):

$$Sh = \frac{k_{bl} d_h}{D_{i,water}} = 1.86\, Re^{1/3}\, Sc^{1/3} \left(\frac{d_h}{L}\right)^{1/3} \tag{4}$$

where d_h is the hydraulic diameter, L a characteristic measure of the module defined by Dotremont et al. (1994) for a similar plate and frame module and $D_{i,water}$ the diffusion coefficient of i in water estimated using the Wilke-Chang correlation (Poling et al. 2001).

For pervaporation of dilute organic solutions, the boundary layer mass transfer resistance for water transport is assumed to be negligible (Ji et al. 1994):

$$J_w = Q_w^m \left(p_w^s \gamma_w x_w - y_w p_p\right) \tag{5}$$

for dilute aqueous solutions activity coefficient and molar fraction of water are approximately equal to 1.

The separation performance of a pervaporation membrane can be described in terms of the permeation flux and the separation factor of the membrane (Huang and Rhim, 1991). The enrichment factor of a given component is the relationship between the concentration in the permeate and the feed:

$$\beta_i = w_{i,p} / w_{i,f} \tag{6}$$

In dilute systems, as aroma recovery systems, the solvent enrichment factor is close to one, so aroma enrichment factors can be considered equal to the corresponding separation factors.

3. Experimental section

3.1. Materials

Pervaporation membrane

The membrane used in this work was a hydrophobic membrane kindly supplied by GKKS Research Center (Germany). This membrane has a selective layer of POMS (polyoctylmethyl siloxane) on a PEI (poly ether imide) support (batch 03/011).

Volatile compounds

The identification of the main volatile components present in the brown crab effluent was performed by using a headspace-solid phase dynamic extraction-gas chromatography/mass spectrometry (HS-SPDE-GC/MS). More than 150 compounds were identified in the brown crab effluent. Among them, seven compounds have been selected for a model aqueous solution of brown crab effluent. The selected volatile compounds belong to different chemical classes: 1-octen-3-ol (Sigma Aldrich, 98 %), 1-penten-3-ol (Sigma Aldrich, 99 %), 3-methylbutanal (Sigma Aldrich, 97 %), hexanal (Sigma Aldrich, 98 %), benzaldehyde (Sigma Aldrich, >=99 %), 2,3-pentadione (Sigma Aldrich, 98 %) and ethyl acetate (Sigma Aldrich, HPLC grade). These compounds are characteristic of seafood flavour: 1-octen-3-ol has been reported to be one of the volatile components widely distributed in fresh and saltwater fish, 1-penten-3-ol contributes to a butter-like odor (although its aroma treshold value is rather high), 3-methylbutanal is one of the most abundant volatile compound in boiled and pasteurized crabmeat, hexanal is one of the most abundant volatiles generated during lipid oxidation at moderate temperatures, benzaldehyde contributes to characteristic cooked crab flavour and ketones such as 2,3 pentadione contribute to the sweet floral, fruity flavour of many crustacean (Cha et al., 1993; Josephson, 1990; Matiella and Hsieh, 1990). Ethyl acetate was also found in the brown crab effluent and it was included in the model solution since could be considered as model molecule (Baudot et al., 1999).

Table 1 summarizes the organoleptic characteristics of the selected volatile compounds including the aroma threshold values (ATV), defined as the lowest concentration in a water solution at which an aroma compound is perceptible. Table 2 lists some thermodynamic properties of the selected compounds, including activity coefficients at infinite dilution and vapor pressure of the volatile compounds. Vapor pressure correlations were obtained or predicted by using Aspen Plus (2008) except for 2,3-pentadione which Antoine constants were obtained from the literature (Soni et al., 2008). Figure 1 shows the vapor pressure of the volatile compounds including water vapor pressure as a function of temperature.

3.2. Feed solutions

Different feed solutions were used in this work. First, pervaporation experiments were performed using pure water as feed solution to check the performance of the POMS membrane. Further, separations of binary mixtures (water/1-octen-3-ol) and multicomponent mixtures were carried out in order to evaluate the influence of some operating variables such as: feed flow rate, feed concentration, feed temperature and permeate pressure on pervaporation performance.

3.3. Pervaporation experiments

The pervaporation experiments were performed under steady state with a plate and frame laboratory stainless steel permeation cell (Sulzer Chemtech®) with an effective membrane area in contact with the feed mixture of 170 cm^2 (Delgado et al., 2009). The temperature of the feed liquid mixture was kept constant (± 0.5 ºC) by using a thermostat to heat the stirred tank feed reactor of 5 L capacity. Permeate pressure was regulated with an air-inlet located between the condensers and the vacuum pump. The chemical stability of the membrane was checked between each experiment, measuring pure water flux at reference operating conditions.

3.4. Sample analysis

Permeate and feed concentrations were measured off-line using a Hewlett Packard (6890) gas chromatograph (GC) equipped with series connected thermal conductivity (TCD) and flame ionization (FID) detectors. Helium, 99.999 % pure, was used as carrier gas. The GC column was a 007 FFAP 25 m × 0.25 mm bonded phase fused silica capillary column. The injector and detectors were at 200 ºC and 250ºC respectively. The oven was operated at programmed temperature, from 40ºC to 220ºC. 1-hexanol was used as internal standard for analysis of the samples.

4. Results and discussion

4.1 Pure water as feed solution

The effect of feed temperature and permeate pressure on membrane performance was studied using pure water as feed solution to check the behaviour of the POMS membrane. Feed temperature was varied in the range 26 ºC to 45 ºC. By increasing feed temperature, water permeation flux also increases mainly due to the increase of saturated water pressure on the feed side of the membrane (Eq. 5). The temperature dependence of water permeation flux, J_{water}, can be expressed by an Arrhenius-type relation:

$$J_{water} = J_{water,o} \exp\left(-E_{a,water}/RT\right) \tag{7}$$

where $E_{a,water}$ is the apparent activation energy of permeation, $J_{water,o}$ the preexponential factor and T the absolute temperature. An apparent activation energy of 46.65 kJ/mol

(Figure 2) was found by fitting water permeation flux obtained in this section (pure water as feed solution) as well as water permeation flux obtained in the pervaporation of volatile compounds dilute aqueous solutions (section 4.3).

Permeate pressure was varied in the range 100 Pa to 1200 Pa. Figure 3 shows the water permeation flux dependence on permeate pressure. This Figure shows experimental data obtained using pure water as feed solution and the results obtained in subsequent studies (section 4.3). Figure 3 shows that by increasing the permeate pressure, water permeation flux decreases as consequence of a decrease in the driving force (Equation 5). Water permeances for the POMS membrane, calculated as the ratio of the permeation flux to the permeant driving force, were constant whatever the feed temperature and permeate pressure considered ($1.95\cdot10^{-7} \pm 1.23\cdot10^{-8}$ $mol s^{-1} m^{-2} Pa^{-1}$ for all the experiments performed in this work).

4.2 Binary feed solution

4.2.1 Boundary layer effect

First, the boundary layer effect was studied in the pervaporation of the binary system water/1-octen-3-ol by varying the feed flow rate between 25 kg/h to 92 kg/h. According to resistance-in-series model when boundary layer is dominant resistance, mass transfer across the membrane increases with feed flow rate due to a decrease of the boundary layer thickness. Figure 4 shows the effect of increasing feed flow rate on partial (water and 1-octen-3-ol) permeation flux. Water and organic permeation fluxes were approximately constant inferring that little concentration polarization takes place. The mass transfer coefficient k_{bl} was calculated according to Sherwood correlation (Eq. 4). The relative significance of the boundary layer mass transfer resistance was estimated less than 2% of the total resistance in the range of feed flow rates studied in this work. However this result must be carefully considered since Olsson and Tragardh (1999a) in their study of the influence of feed flow velocity on pervaporative aroma recovery pointed out that Sherwood correlation could overestimates the mass transfer coefficient of the liquid feed boundary layer.

4.2.2. Effect of feed concentration

The effect of organic feed concentration was studied for water/1-octen-3-ol by varying the volatile feed concentration in the range of 0.1 to 10 ppm. By increasing the concentration of the volatile component in the feed solution, organic partial permeation flux increases. A linear dependence of organic permeation flux can be assumed in the range of concentrations studied in this work ($r^2 = 0.97$). However, water permeation flux remained constant whatever the feed concentration (within the experimental error) and similar to the values obtained when using pure water as feed solution. The mean value found for 1-octen-3-ol enrichment factor was 37 ± 5.

4.3 Multicomponent feed solution

Finally the effect of feed concentration, feed temperature and permeate pressure was study in the pervaporation of a feed model solution consisting of seven volatile compounds: 1-octen-3-ol, 1-penten-3-ol, 3-methylbutanal, hexanal, benzaldehyde, 2,3-pentadione and ethyl acetate.

4.3.1. Effect of feed concentration

The feed concentration of all the organic compounds studied in this work was varied in the range of 0.1 to 10 ppm at a fixed feed temperature (26ºC) and permeate pressure (300 Pa). Volatile organic concentration found in the brown crab effluent was rather low (less than 2 ppm). A wider range has been studied to minimize errors in the volatile organic compound determination. Figure 5 shows an acceptable linear relationship between organic permeation flux and feed concentration ($r^2 > 0.95$, except for benzaldehyde and 3-methylbutanal, $r^2 = 0.93$). This behaviour indicates that a constant normalized permeation flux (permeance) can be assumed in the studied concentration range. Figure 6 shows the membrane permeance for the volatile compounds studied in this work as a function of organic concentration in the feed. The greatest deviations were shown for benzaldehyde. The lower values of the permeances correspond to 3-methylbutanal and ethylacetate, these are the organic compounds with the greater vapour pressure. The enrichment factor for the volatile compounds was independent of concentration in the range investigated in this work. The observed tendency of enrichment factor was the following: $\beta_{\text{1-octen-3-ol}}$ (≈121) > $\beta_{\text{benzaldehyde}}$ (≈93) > $\beta_{\text{1-penten-3-ol}}$ (≈25) > β_{hexanal} (≈22) > $\beta_{\text{2,3-pentanedione}}$ (≈7) ≈ $\beta_{\text{ethylacetate}}$ (≈7) > $\beta_{\text{3-methylbutanal}}$ (≈5).

Water permeation flux remains constant and equal to the flux of pure water (within the experimental error) whatever the feed concentration of the different aroma compounds.

Compared to the binary system previously studied 1-octen-3-ol shows an increase in permeability in model multicomponent mixtures. This indicates that the presence of other organic compounds in the feed solution can affect the membrane selectivity due to interactions between the different aroma compounds. In this case a positive effect was observed in the 1-octen-3-ol permeation. Other studies of the pervaporation of organic compounds multicomponent mixtures (Isci et al., 2006; Kanani et al., 2003; Sampranpiboon et al., 2000) have also observed positive or negative interactions between the permeating aroma compounds. Isci et al. (2006) explained that higher fluxes than expected can be obtained when a permeant of low diffusivity is dragged through the membrane polymer by a permeant of higher diffusivity; the opposite can also happen.

4.3.2. Effect of feed temperature

Feed temperature is an important operating variable since it affects the feed/membrane characteristics and the driving force of the process. The operating temperature was changed in the range 26 ºC to 35.7 ºC at a fixed permeate pressure (300 Pa) and different fixed feed concentration (0.1, 5 and 10 ppm). Moderate feed temperature is recommended in the study of pervaporation of flavour compounds to avoid any damage to heat-sensitive compounds. (She and Hwang, 2006). Figure 7 shows the effect of temperature on volatile compounds permeation fluxes at an organic feed concentration of 10 ppm for all the volatile compounds. For all the organic compounds, when the temperature increases the organic permeation flux increases. The variation of the volatile compounds permeation flux with temperature was found to follow an Arrhenius type relationship (Eq. 7). Apparent activation energy for permeation of aroma compounds follows the order: $E_{a,benzaldehyde}$ (49.47 kJ/mol) < $E_{a,1\text{-}octen\text{-}3\text{-}ol}$ (58.64 kJ/mol) < $E_{a,hexanal}$ (79.55 kJ/mol) < $E_{a,1\text{-}penten\text{-}3\text{-}ol}$ (84.77 kJ/mol) < $E_{a,ethylacetate}$ (86.81) < $E_{a,3\text{-}methylbutanal}$ (87.66 kJ/mol) < $E_{a,2,3pentadione}$ (155.01 kJ/mol). The apparent activation energy found for all volatile compounds is higher than that of water ($E_{a,water}$ = 46.65 kJ/mol). A higher value of the apparent activation energy indicates a more sensitive behaviour towards temperature changes, inferring that water permeation flux is less temperature dependence than that of volatile compounds. Therefore, the enrichment factor of all volatile compounds increases with an increase in the feed temperature. According to the values found for the apparent activation energy this trend was more noticeable for the most volatile component than for the less volatile components considered in this work. Figure 8 shows the enrichment factor at the three temperatures studied in this work at a fixed feed concentration of 10 ppm for the volatile compounds. Similar behaviour has been described in the literature in the recovery by pervaporation of different volatile aroma compounds through different pervaporation membranes (Aroujalian and Raisi, 2007; Olsson and Trägardh, 1999b; Raisi et al., 2008). The results found in this section show a strong dependence on temperature for 2,3-pentadione. Further studies are necessary to confirm such behaviour.

With increasing temperature, the driving force increases because of the increasing vapour pressure, and therefore the permeate flux will also increase (see Eq. 1). Additionally, an increase in the operating temperature causes an increase in the motion of the polymer chains improving the diffusion of the permeant molecules. Figure 9 shows the ratio of partial permeation fluxes obtained at 35.7 ºC and 26 ºC for all the volatile compounds and water. According to Olsson and Trägardh (1999b) the contribution from improved diffusion and increasing driving force to the increase of partial permeation flux has been also shown. This Figure shows that for water and the less volatile components (benzaldehyde, 1-octen-3-ol and 1-penten-3-ol) the increase in partial permeation flux is mainly due to an increase in the driving force. However the contribution due to an increasing diffusion becomes important for the more volatile compounds.

Enrichment factor values seem to decrease with the apparent activation energy values. The activation energy that characterizes the temperature dependence of the membrane can be estimated by subtracting the heat of vaporization (ranging from 35 $kJ \cdot mol^{-1}$ for ethyl acetate to 57 $kJ \cdot mol^{-1}$ for 1-penten-3-ol) from the calculated apparent activation energy (Feng and Huang, 1996). Activation energy of aroma compounds follows the order: $E_{a,benzaldehyde}$ (-0.17 kJ/mol) < $E_{a,1\text{-}octen\text{-}3\text{-}ol}$ (8.26 kJ/mol) < $E_{a,1\text{-}penten\text{-}3\text{-}ol}$ (27.72 kJ/mol) <

$E_{a,hexanal}$ (36.73 kJ/mol) < $E_{a,3\text{-}methylbutanal}$ (50.23 kJ/mol) < $E_{a,ethylacetate}$ (51.57) < $E_{a,2,3pentadione}$ (116.82 kJ/mol). From the values of activation energy, it could be concluded that sorption contributes more to permeation of 1-octen-3-ol and benzaldehyde molecules (the more hydrophobic compounds and less volatile). In contrast, the permeation for the rest of the volatile compounds studied in this work seems to be a diffusion dominating process.

4.3.3. Effect of permeate pressure

Permeate pressure is another operating parameter that affects the pervaporation performance as well as the operating cost of the process (Raisi et al., 2008). Different behavior was observed for organic permeation fluxes when varying permeate pressure in the range studied in this work (100 Pa – 1800 Pa). Trifunovic et al. (2006) state that in general components that are less volatile are more sensitive to changes in permeate pressure than compounds with higher volatility due to their smaller driving force. Figure 10 presents the effect of permeate pressure on the enrichment factor of the aroma compounds considered in this work. For the low volatile components (1-octen-3-ol and benzaldehyde) the enrichment factor decreases as permeate pressure increases. However, other components such as 1-penten-3-ol, hexanal and 2,3-pentadione are less sensitive to changes in permeate pressure. Figure 10 shows that the enrichment factor of the components with higher equilibrium vapour pressure than water (3-methylbutanal and ethyl acetate) tends to increase as permeate pressure increases. These results agree with other findings that appear on literature. According to Aroujalian and Raisi (2007) if the less volatile component is the more rapidly permeating species, selectivity decreases as permeate pressure increases. On the other hand, if the more rapidly permeating species are also the more volatile, selectivity increases as permeate pressure increases. As pointed out by Wijmans et al. (1996), this indicates a unique characteristic of pervaporation process since separation can be improved by decreasing the driving force of the process.

5. Conclusions

In this work, the recovery of volatile components from a model solution was performed by pervaporation with a POMS membrane. Pervaporation seems to be a promising technique for the recovery of aroma compounds from brown crab effluent. POMS membrane has been able to separate the organic compounds although organic partial permeation fluxes were not very high. A constant water permeance was observed for all the experiments carried out in this study. The membrane used in this work has shown higher selectivity towards the less volatile components. Organic permeation fluxes increase with feed concentration as a consequence of a higher driving force for the mass transport. In general partial permeation fluxes and enrichment factors increase as the feed temperature increases. However different behavior was observed for organic permeation fluxes with permeate pressure. As permeate pressure increases enrichment factor of the less volatile component was found to decrease, however for the most volatile components enrichment factors tend to increase by decreasing the driving force of the process. Operating conditions can be optimized to obtain permeates with a maximum organleptic quality in its aroma profile. Further research is needed to account the influence of other substances present in brown crab effluent such as salt content.

Nomenclature

d_h = hydraulic diameter, m

D = diffusion coefficient, $m^2 \cdot s^{-1}$

E_a = apparent activation energy of permeation, $kJ \cdot mol^{-1}$

J = mass permeation flux, $g \cdot s^{-1} \cdot m^{-2}$

k_{bl} = liquid boundary layer mass transfer coefficient, $m \cdot s^{-1}$

L = characteristics of the module, m

p = pressure, Pa

Q_{OV} = pressure-normalized permeation flux, $g \cdot s^{-1} \cdot m^{-2} \cdot Pa^{-1}$

Q_m = pressure-normalized permeation flux across the membrane, $g \cdot s^{-1} \cdot m^{-2} \cdot Pa^{-1}$

R = gas constant, $kJ \cdot mol^{-1} K^{-1}$

T = absolute temperature, K

x, y = mol fraction

ρ = total mass volume concentration of the feed, $g \cdot m^{-3}$

γ = activity coefficient

β = enrichment factor

upperscripts

i = component

m = membrane

p = permeate

s = saturation

Acknowledgments

Financial support from the MICINN through CTQ2008-04999-PPQ is gratefully acknowledged. R. Martinez acknowledges the JCyL Education Ministry.

References

Aroujalian, A., & Raisi A. (2007). Recovery of volatile aroma components from orange juice by pervaporation. J. Membr. Sci., 303, 154-161.

Aspen Plus V7.1 (2008) Aspen Technology, Inc., 2008.

Baudot, A., Souchon, I., & Marin, M. (1999). Total permeate pressure influence on the selectivity of the pervaporation of aroma compounds. J. Membr. Sci., 158, 167-185.

Blume, I., Wijmans, J.G., & Baker, R. W. (1990). The separation of dissolved organics from water by pervaporation. J. Membr. Sci., 49, 253-286.

Cha, Y.J., Cadwallader, K.R., & Baek, H.H. (1993). Volatile flavor components in snow crab cooker effluent and effluent concentrate. J. Food Sci., 58, 525-530.

Delgado, P., Sanz, M.T., & Beltrán, S. (2009). Pervaporation of the quaternary mixture present during the esterification of lactic acid with ethanol. J. Membr. Sci., 332, 113-120.

Dotremont, C., Van den Ende, S., Vandommele, H., & Vandecasteele, C. (1994). Concentration polarization and other boundary layer effects in the pervaporation of chlorinated hydrocarbons. Desalination, 95, 91-113.

Feng, X.; & Huang, R.Y.M. (1996). Estimation of activation energy for permeation in pervaporation processes. J. Membr. Sci., 118, 127-131.

Flavor-Base Professional (2007), Lefingwell & Associates.

García, V., Diban, N., Gorri, D., Keiski, R., Urtiaga, A., &. Ortiz, I. (2008). Separation and concentration of bilberry impact aroma compound from dilute model solution by pervaporation. J. Chem. Technol. Biotechnol., 83, 973-982.

Huang, R.Y.M, & Rhim, J.W. (1991) Separation characteristics of pervaporation membrane separation processes. In Elsevier (Ed.), *Pervaporation Membrane Separation Processes* (pp. 111-180). Amsterdam.

Isci, A., Sahin, S., & Sumnu, G. (2006). Recovery of strawberry aroma compounds by pervaporation. J. Food Eng, 75, 36-42.

Ji, W., Hilalyb, A., Sikdarb, S.K., & Hwang, S.T. (1994). Optimization of multicomponent pervaporation for removal of volatile organic compounds from water. J. Membr. Sci., 97, 109-125.

Josephson, D.B. (1991). Seafood. In Marcel Dekker (Ed.), *Volatile compounds in Foods and Beverages* (pp. 179-202). New York.

Kanani, D.M., Nikhade, B.P., Balakrishnan, P., Singh, G., & Pangarkar, W.G. (2003). Recovery of valuable tea aroma components by pervaporation. Ind. Eng. Chem. Res., 42, 6924-6932.

Matiella, J., & Hsieh, T.C. (1990). Analysis of crabmeat volatile compounds. J. Food Sci., 55, 962-966.

Olsson, J., & Tragardh, G. (1999a). Influence of feed flow velocity on pervaporative aroma recovery from a model solution of apple juice aroma compounds. J. Food Eng., 39, 107-115.

Olsson, J., & Tragardh, G. (1999b). Influence of temperature on membrane permeabilibity during pervaporative aroma recovery. Sep. Sci. Technol., 34, 1643-1659.

Poling, B.E., Prausnitz, J.M., & O’Connell, J.P. (2001). Difussion Coefficients. In McGraw-Hill (Ed.), *The Properties of Gases and Liquids* (pp. 11.1-11.55). New York.

Raisi, A., Aroujalina, A., & Kaghazchi, T. (2008). Multicomponent pervaporation process for volatile aroma compounds recovery form pomegranate juice. J. Membr. Sci., 322, 339-348.

Sampranpiboon, P., Jiraratananon, R., Uttapap, D., Feng, X., & Huang, R.Y.M. (2000). Separation of aroma compounds from aqueous solution by pervaporation using polyoctylmethylsiloxane (POMS) and polydimethylsiloxane (PDMS) membranes. J. Membr. Sci., 174, 55-65.

She, M., & Hwang, S.-T. (2006). Recovery of key components from real flavour concentrates by pervaporation. J. Membr. Sci., 279, 86-93.

Soni, M., Ramjugernath, D., & Raal, J.D. (2008). Vapor-Liquid Equilibrium for binary systems of 2,3-pentanedione with diacetyl and acetone. J. Chem. Eng. Data, 53, 745-749.

Trifunovic, O., & Trägardh, G. (2006). Mass transport of aliphatic alcohols and esters through hydrophobic pervaporation membranes. Sep. Purif. Technol., 50, 51-61.

Trifunovic, O., Lipnizki, F., & Tragardh, G. (2006). The influence of process parameters on aroma recovery by hydrophobic pervaporation. Desalination, 189, 1-12.

Wijmans, J.G., Athayde, A.L., Danield, R., Ly, J.H., Kamaruddin, H.D., & Pinnau, I. (1996). The role of boundary layers in the removal of volatile orgnacis compounds from water by pervaporation. J. Membr. Sci., 109, 135-146.

Table 1. Aroma compounds used in the model solution (Flavor-Base Professional, 2007).

Aroma compound	Organoleptic characteristics	ATV, ppb
1-Octen-3-ol	Very strong, sweet, earthy mushroom odor and taste	1.0
1-Penten-3-ol	Pungent, grassy, alliaceous-like, green vegetable, fruity taste	400
3-Methylbutanal	Powerful, penetrating, cheesy-sweaty-fruity in dilution	0.2-2
Hexanal	Strong, penetrating, fatty-green, grassy unripe fruit odor	4.5
Benzaldehyde	Odor of bitter almond oil, characteristic sweet cherry taste	350
2,3-Pentadione	Oily-buttery, fatty odor, butter, cream, milk taste	30
Ethyl Acetate	Ethereal, sharp, wine-brandy like odor	5.0

Table 2. Physicochemical properties of the volatile compounds

Compound	1-Octen-3-ol	1-Penten-3-ol	3-Methylbutanal	Hexanal	Benzaldehyde	2,3-Pentadione	Ethyl acetate
MW	128.2	86.1	86.1	100.2	106.1	100.1	88.1
BP (ºC)	174-5	114.4	92.5	128.3	178.8	108	77.1
p^s (26ºC), Pa	65	1348	7035	1540	181	2918	13045
γ^∞(26ºC)	4955.4	17.0	164.6	1047.2	273.7	282.4	75.3
VM^{BP}(cc/mol)	186.6	117	118.9	140.0	118.6	121	106.3

List of Figure Caption

Figure 1. Vapor pressure of water and volatile compounds as a function of temperature.

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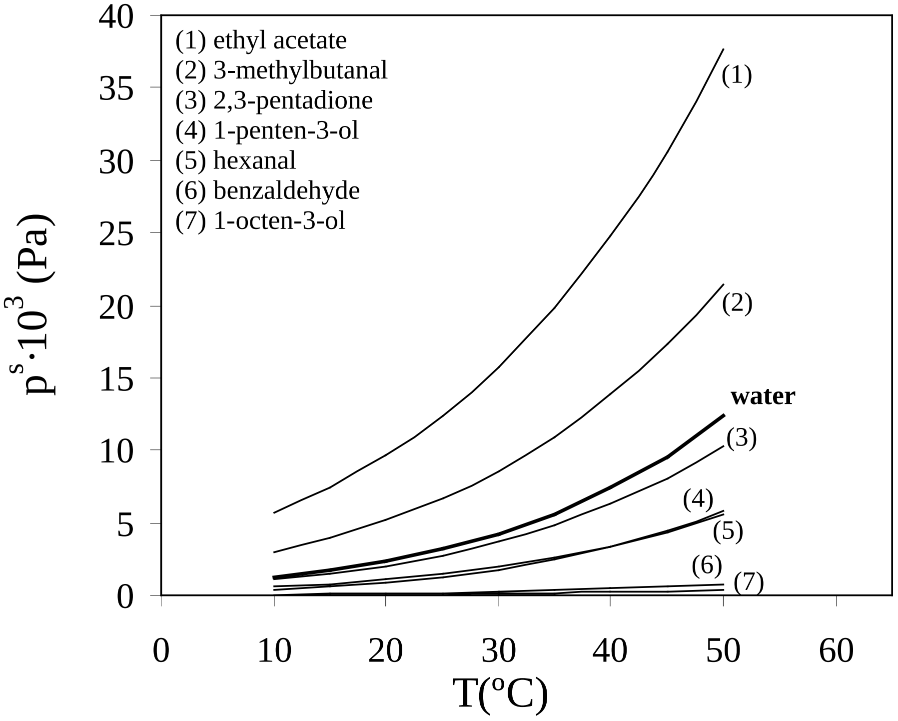

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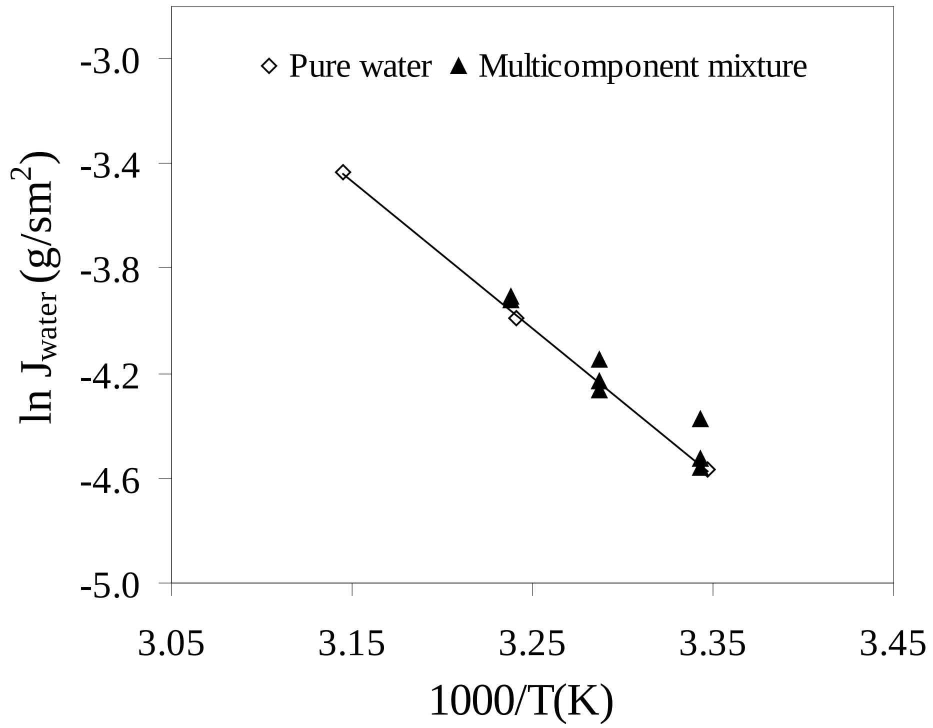


Figure 2. Effect of temperature on water permeation flux (p_p = 300 Pa).

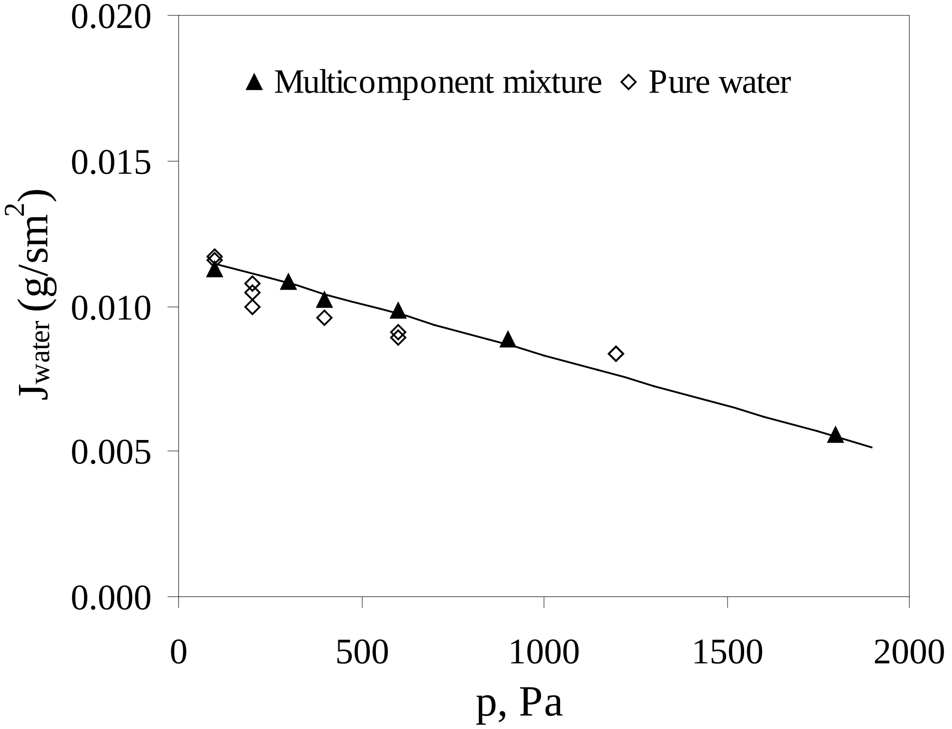


Figure 3. Effect of permeate pressure on water permeation flux (T = 26ºC).

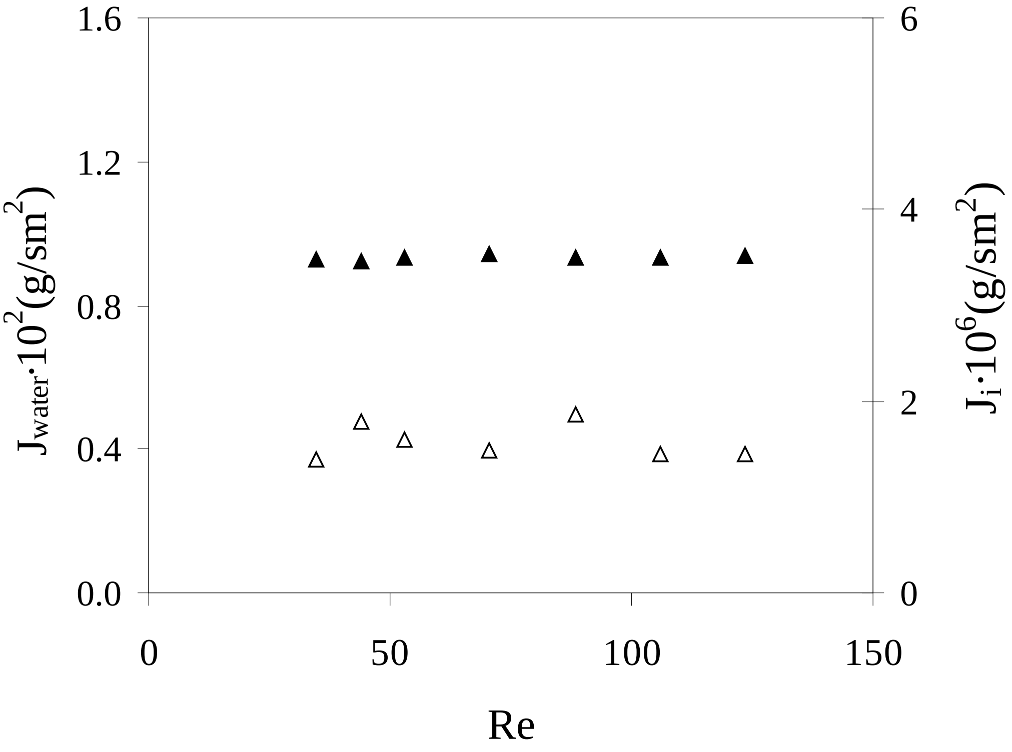


Figure 4. Water (▲) and 1-octen-3-ol (i, Δ) permeation flux at different Reynolds (p_p = 400 Pa, T = 26ºC, $C_{i,feed} \approx 5$ ppm).

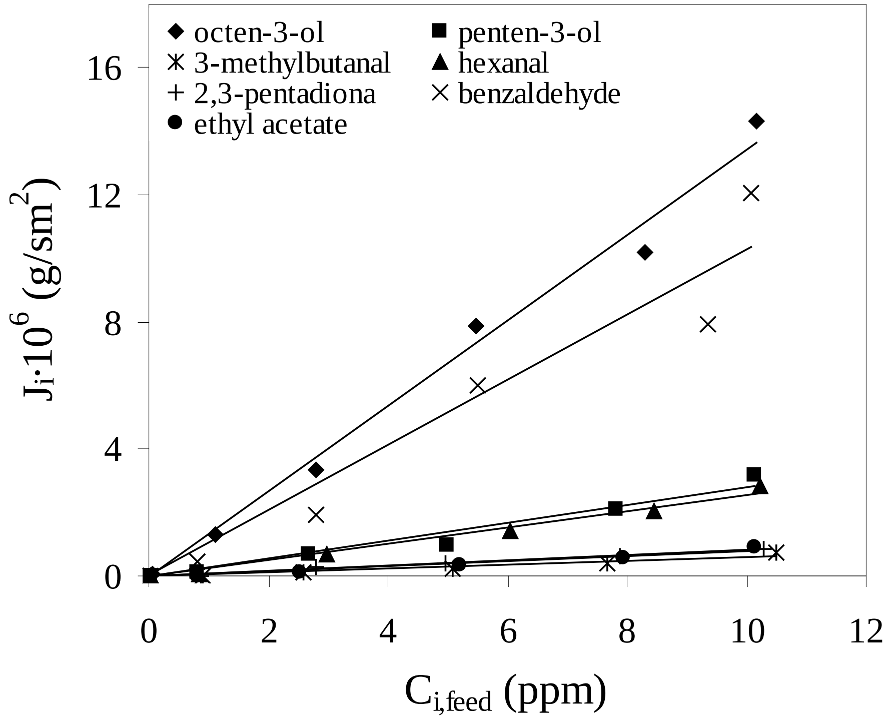


Figure 5. Effect of volatile feed concentration on volatile compound permeation flux (T = 26 ºC, p_p = 300 Pa).

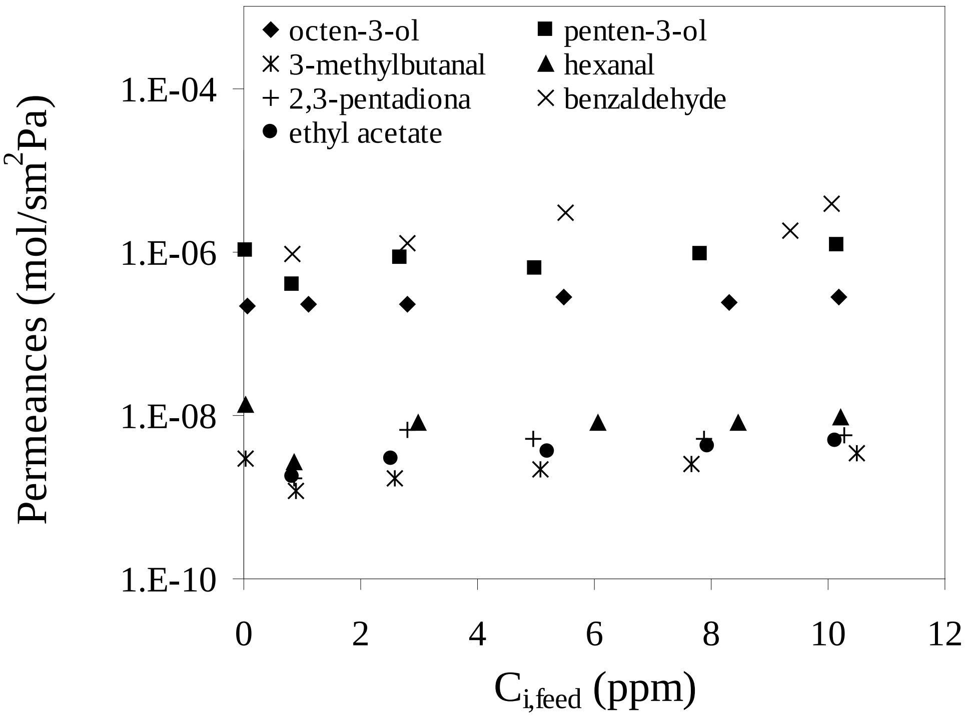


Figure 6. Volatile compound permeance as a function of volatile feed concentration (T = 26 ºC, p_p = 300 Pa).

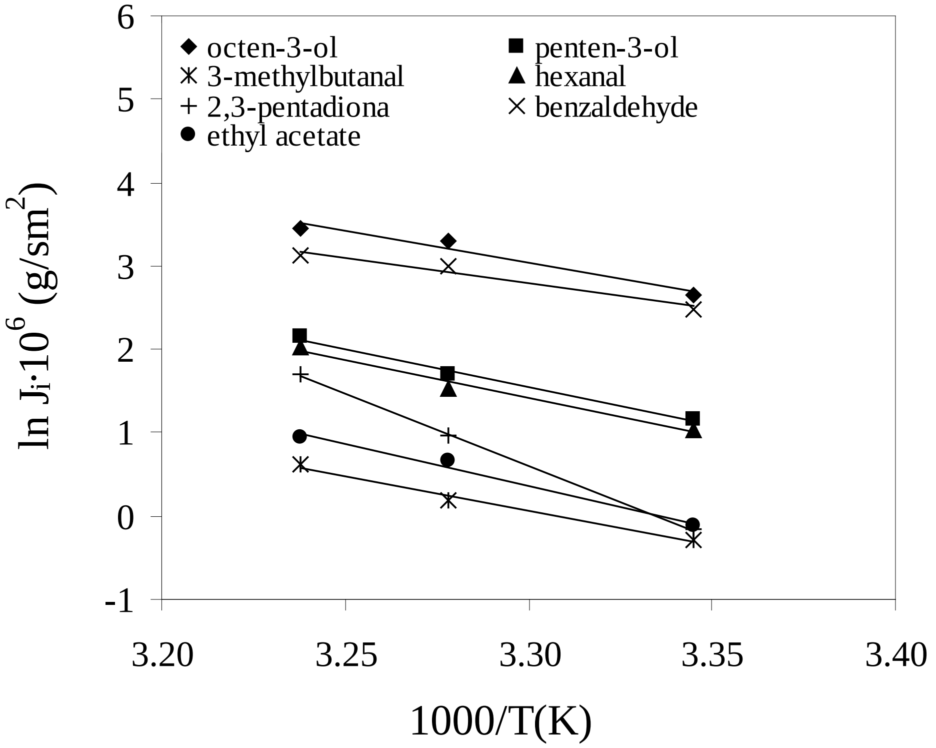
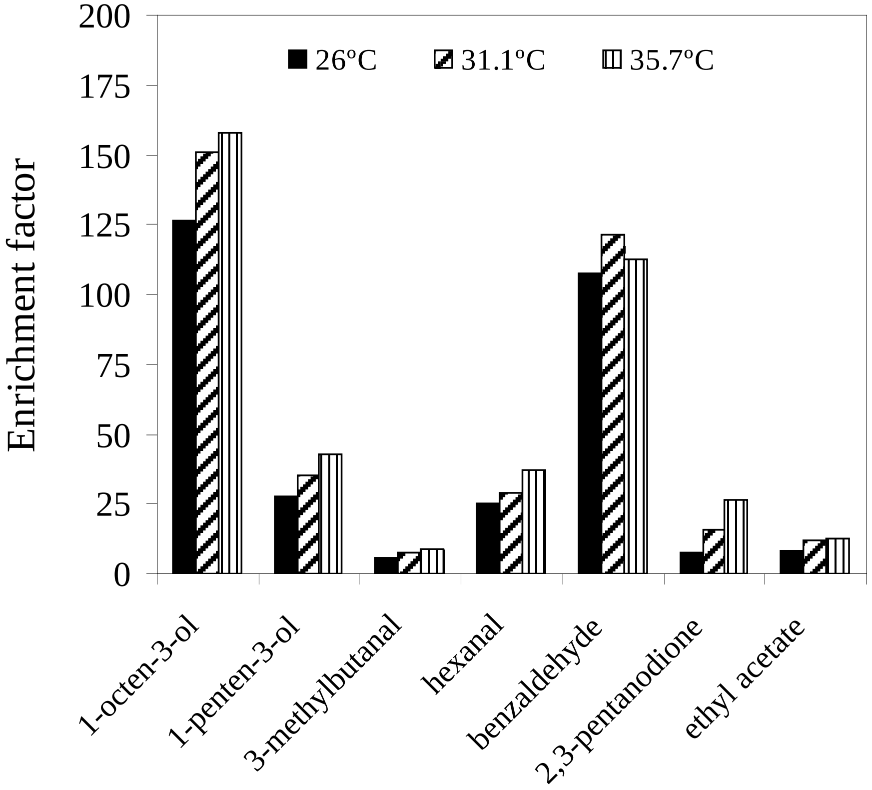


Figure 7. Effect of feed temperature on volatile compound permeation flux ($C_{i,\ feed} \approx$ 10 ppm, p_p = 300 Pa).



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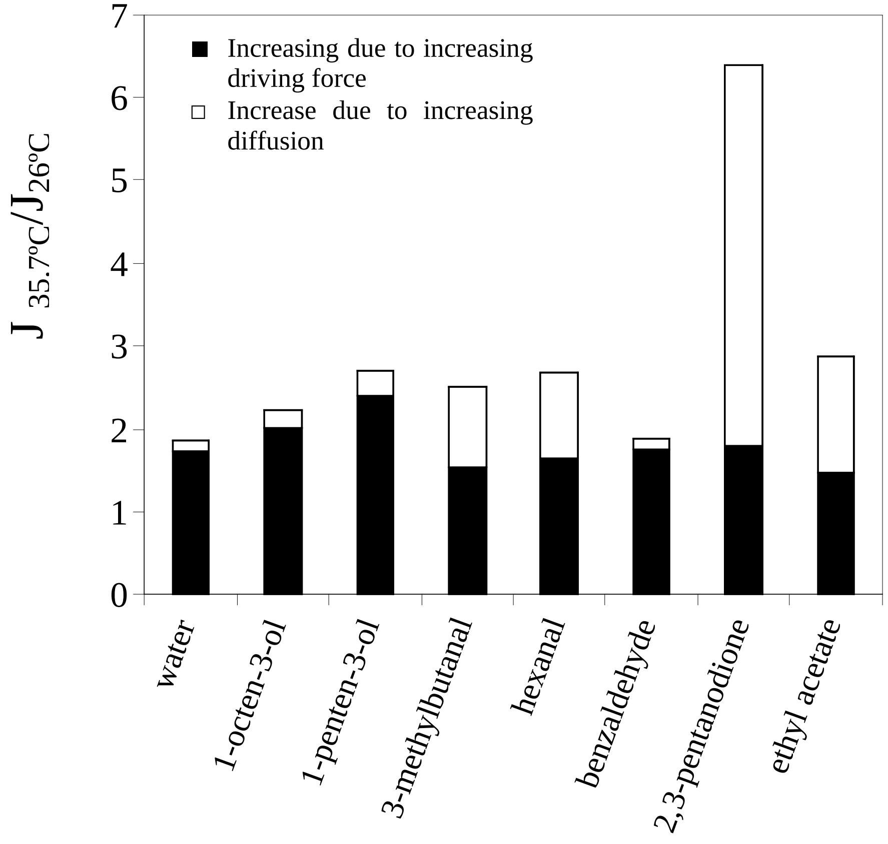

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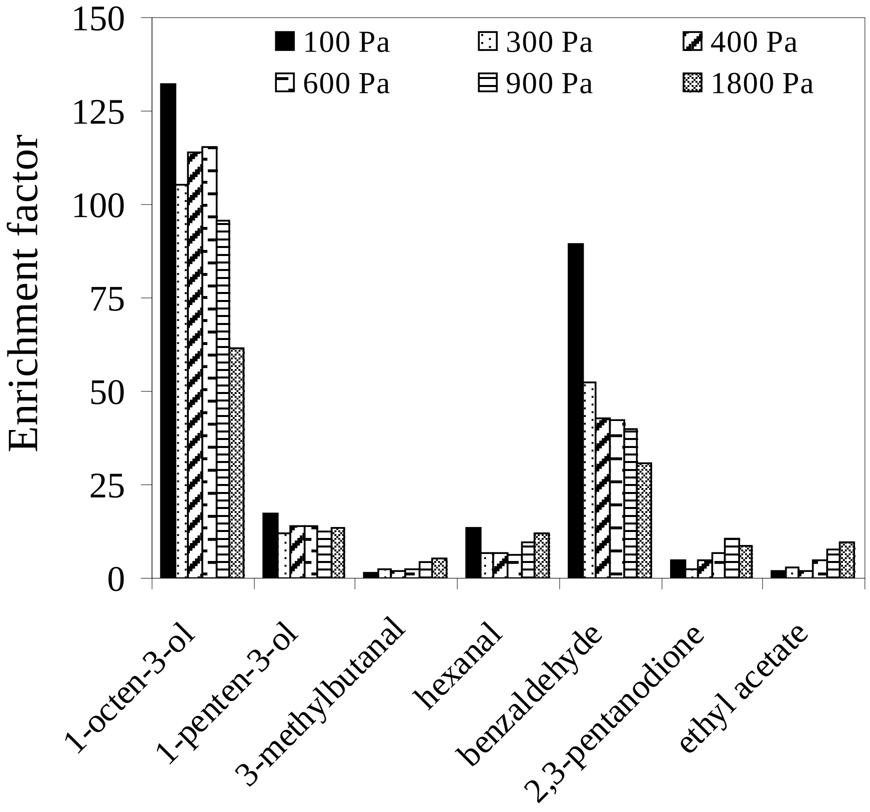

Figure 10. Enrichment factor of volatile compound at different operating permeate pressure ($C_{i,feed} \approx 10$ ppm, T = 26 ºC).