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Pervaporation process of coffee volatile compounds with PDMS membrane

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Abstract

Pervaporation experiments were performed with diluted aqueous solutions of coffee aroma volatile compounds (benzaldehyde and acetic acid) using a PDMS membrane. Binary solutions of benzaldehyde (BZ-water), acetic acid (AA-water), and a ternary solution (BZ-AA-water) were used as feed to investigate the effects of temperature (20, 30, and 40°C), pressure (270, 530, and 800 Pa), and feed composition (20, 40, and 60 ppm) on the process. The dependence of permeation fluxes with the temperature was expressed by the non-linear Arrhenius equation for all assays. Only the BZ enrichment factor in binary solutions increased with temperature. The increase in feed concentration caused a linear rise in individual permeation fluxes; however, it did not influence the membrane selectivity to the binary solutions. The individual permeation fluxes and enrichment factor for both BZ and AA were negatively influenced by the presence of another organic molecule.

Introduction

The coffee beverage is one of the most popular beverages in the world, is obtained by the infusion of roasted and grounded coffee beans; and its consumption has been growing on a daily basis (Cheong *et al.,* 2013). Brazil is the world's main coffee producer and the second-largest coffee consumer.

Aroma is an important attribute that defines the acceptability of consumers for coffee products. Many functional groups such as aldehydes, ketones, esters, mercaptans, sulphides, disulphides, thiophenes, and thiazoles; and over 1,000 volatile compounds have been identified and reported as coffee aroma constituents (Buffo and Cardelli-Freire, 2004; Raisi and Aroujalian, 2011). The contribution of each compound to the final aroma depends on its concentration and the sensory perception limit, thus some of these substances could contribute either positively or negatively to the product sensory attributes (Amstalden *et al.,* 2001).

Coffee production is crucial for obtaining a quality product, with roasting as the main step due to the formation of compounds responsible for the characteristic of coffee aroma and taste (Buffo and Cardelli-Freire, 2004; Esquivel and Jiménez, 2012). Roasted coffee is milled and used to obtain the soluble coffee. During extraction, another processing step is usually carried out by thermal evaporation, and a loss of volatile compounds relevant to the aroma composition occurs, thus resulting in a lower quality product. The re-incorporation of volatile compounds during the soluble coffee production process is an alternative to re-increase the aromatic perception and benefit of the product.

Aroma compound recovery is usually accomplished using thermal processes, which could lead to undesirable changes in aroma composition as well as high energy costs. Some processes have been investigated for aroma compound recovery, more specifically for coffee, such as adsorption (Zuim *et al.,* 2011; Carpiné *et al.,* 2013), supercritical extraction (Lucas *et al.,* 2004; Lucas and Cocero, 2006), wet grinding (Baggenstoss *et al.,* 2010), nanofiltration (Pan *et al.,* 2013), and pervaporation (Weschenfelder *et al.,* 2015).

Pervaporation is an attractive separation process using membrane, mainly due to its high selectivity and allowing for operation under moderate temperatures. Its application has been studied on fruit juice and beverage aroma recovery (Peng *et al.,* 2003; Isci *et al.,* 2006; Aroujalian and Raisi, 2007), alcoholic beverages (Karlsson *et al.,* 1995; Catarino *et al.,* 2009), dairy flavours (Overington *et al.,* 2008; 2011), and seafood (Martínez *et al.,* 2013).

Some coffee aroma pervaporation studies have been found in the literature (Bizzo *et al.,* 2008; Weschenfelder *et al.,* 2015). In these studies, the performance of pervaporation process for aroma compound recovery was evaluated using coffee beverage and industrial soluble coffee. However, a systematic evaluation of the volatile components affecting the coffee beverage is required. This research ought to be carried out with a view towards yield and selectivity of the coffee aromas involved since not all volatile

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compounds found in coffee offer a pleasant aroma to the final consumer (Cheong *et al.,* 2013; Weschenfelder *et al.,* 2015).

In this context, the present work aimed at evaluating the pervaporation process on diluted aqueous solutions of two coffee aroma compounds. The effects of temperature, concentration, feed composition, and permeate pressure on permeation flux and selectivity were investigated. The compounds chosen in the present work were benzaldehyde and acetic acid, which possess positive and negative influences on the sensorial quality of coffee.

Theory

Pervaporation is a membrane separation process where a change from liquid to gaseous phase occurs during permeation of a component through the membrane. In pervaporation, according to Feng and Huang (1997), the solution-diffusion model is the main mass transport mechanism, consisting of three steps: (i) selective sorption at the feed side of the membrane, (ii) diffusion of the permeant through the membrane, and (iii) desorption of the permeant in the vapor phase on the permeate side of the membrane.

The performance of the pervaporation process is evaluated in terms of flux and selectivity. The permeation flux J (kg/m^{2}h) that quantitatively expresses the yield of the operation is calculated using Eq. 1:

$$J=\frac{m_p}{A_m} \qquad \text{(Eq. 1)}$$

where, m_p (kg) = mass permeated through the membrane, A_m (m^2) = permeation area, and t (h) = operating time.

The selectivity of the membrane is expressed by the separation factor ($\alpha i/j$) or enrichment factor (β i). The separation factor indicates the preferential permeation of the process for component i as compared to component j. It is obtained by the concentration ratio of each component in the permeate (C^P) and feed (C^F) (Pereira *et al.,* 2006) as shown in Eq. 2:

$$\alpha_i\text{T}_j=\frac{C_i^P\,/\,C_j^P}{C_i^F\,/\,C_j^F} \qquad \text{(Eq. 2)}$$

The enrichment factor represents the ability of the membrane to concentrate component i by the ratio (Peng *et al*., 2003) as shown in Eq. 3:

$$\beta_i=\frac{C_i^P}{C_i^F} \qquad \text{(Eq. 3)}$$

The term βi is most conveniently used with highly diluted feed solutions (Feng and Huang, 1997).

The mass transfer driving force is generated by the chemical potential gradient between the feed and permeate phases, represented in terms of either concentration difference or partial pressure. Considering an ideal diffusion of solute across the membrane, the flux of component i (J_i) could be described by Fick's first law (Isci *et al.,* 2006) as shown in Eq. 4:

$$J_i=\frac{D_i(C_{io}\text{-}C_{il})}{l} \qquad \text{(Eq. 4)}$$

where, D_i (m^2/s) = diffusion coefficient of component i in the polymer membrane, l (m) = thickness of the membrane, C_{io} and C_{il} (kg/m^3) = component i concentrations at the feed/membrane interface and the membrane/permeate interface, respectively.

The terms of concentration could be written as a function of partial pressures as shown in Eqs. 5 and 6:

$$C_{i0}=S_ip_{i0} \qquad \text{(Eq. 5)}$$

$$C_{il}=S_ip_{il} \qquad \text{(Eq. 6)}$$

where, p_{iO} and p_{il} (Pa) = partial pressures of component i in the feed and in the permeate, respectively, and S_i (kg/m^{2}Pa) = the sorption coefficient. The combination of Eqs. (4), (5) and (6) results in Eq. 7:

$$J_i=\frac{D_iS_i(p_{i0}\text{-}p_{il})}{l}=\frac{P_i(p_{i0}\text{-}p_{il})}{l} \qquad \text{(Eq. 7)}$$

where the product D_iS_i is defined as permeability, P_i (m^2/s), of component i in the membrane.

Assuming equilibrium in the sorption of solute i between the liquid bulk feed and the membrane surface, S_i could be written as Eq. 8 (Isci *et al.,* 2006):

$$S_i=\frac{C_{i0}}{C_{i,bulk}} \qquad \text{(Eq. 8)}$$

where $C_{i,bulk}$= concentration of component i in the bulk liquid. If the vacuum applied on the permeate side is strong, it is assumed that all solute particles diffusing across the membrane are instantly removed on the permeate side; then C_{il} could be taken as zero. Thus, Eq. 4 could be rewritten as Eq. 9:

$$J_i=\frac{D_iS_i\,(C_{i,bulk})}{l}=\frac{P_i\,(C_{i,bulk})}{l} \qquad \text{(Eq. 9)}$$

The permeate flux increases exponentially, following an Arrhenius type variation, as shown in Eq. 10:

$$J_i = J_0\, exp\left(\frac{-E_a}{RT}\right) \quad \text{(Eq. 4)}$$

where, J_0 (mol/m^{2}s) = pre-exponential factor, E_a (kJ/mol) = apparent activation energy of permeation, R = universal gas constant, and T (K) = absolute temperature.

The apparent activation energy is a parameter that describes the effect of overall temperature on permeation flux (Olsson and Tragardh, 1999). In the literature, E_a has been estimated from the angular coefficient from ln J vs. 1/T plot (Feng and Huang, 1996). However, the non-linear equation was used in the present work to project the value of this parameter, since according to Weschenfelder *et al.* (2015), projecting the correct E_a values through the Arrhenius equation linearisation is a laborious task due to the strong dependence between this parameter and the pre-exponential factor of the equation.

Materials and methods

Feed solutions

Benzaldehyde (CAS 100-52-7) and acetic acid (CAS 64-19-7) were purchased from Sigma-Aldrich (Germany) at ≥ 99% purity. Pervaporation experiments were conducted with pure water as feed in order to evaluate the membrane performance. Then, benzaldehyde-water (BZ-water) and acetic acid-water (AA-water) binary solutions, and BZ-AA-water ternary solutions at different concentrations were used to optimise the operating parameters of the pervaporation process. All solutions were prepared with Milli-Q® (Germany) grade demineralised water .

Membrane

A polymeric hydrophobic membrane was used in all the pervaporation experiments containing a polydimethylsiloxane (PDMS) functional layer and polyethylene terephthalate (PET) support layer with 3 µm thickness and 50 cm^2 effective permeation area (Pervatech BV, the Netherlands).

Pervaporation experiments

For the pervaporation assays, 3.5 L of the solution was prepared at the time of its use, and placed in the 4-L jacketed feed tank coupled to a temperature-controlled bath (Quimis, Brazil) at ± 0.2°C. The feed solution was taken to the stainless-steel plate and frame-type pervaporation module by a flux-controlled diaphragm pump (Bomax, Brazil). Following temperature stabilisation, a vacuum pump (RV12 model, Edwards, West Sussex, UK) was powered. A digital vacuum pressure gauge (VDR-920 model, Instrutherm, Brazil) coupled to the outlet of the pervaporation module was used to control the vacuum, and controlled by a needle valve. The permeate was condensed in a glass cold trap (Corning model, USA) immersed in liquid nitrogen (-196°C).

Prior to each assay, the feed solution recirculated through the system for 2 h in order to stabilise the flux through the membrane and to reach steady-state, after which the cold trap was changed, and the process was initiated. The retentate flux was redirected to the feed tank, allowing continuous feeding. The feed concentration was assumed to be constant throughout the entire operation due to the large solution volume used in the feed tank as compared to the small amount of permeate recovered.

The samples were collected in triplicate at 1 h intervals. The collected permeate mass was determined on the analytical balance. The samples were stored in labelled amber glass flasks, and kept at -18°C until analysis.

A study by Weschenfelder *et al.* (2015) using this pervaporation unit pointed out that the concentration polarisation phenomenon was not observed at flux rates between 1.0 and 3.0 L/min. Thus, all the assays were performed at a fixed 3.0 L/min feed flux rate.

New membranes were conditioned before the pervaporation assays by recirculating 1.0 L of Milli-Q water at 30°C for 10 h under an 800 Pa vacuum. 10 h was deemed sufficient for pre-swelling of the membrane, to allow for a steady-state operation. Assays using Milli-Q water as feed solution were performed and used as a reference to verify membrane stability.

In the present work, temperature, feed concentration, and permeate pressure effects on flux and selectivity were determined. First, three temperatures (20, 30, and 40°C) were studied at three pressures (270, 530, and 800 Pa) with BZ-water and AA-water solutions at 40 ppm each. Then, the feed concentration of the binary solutions was ranged from 20 to 60 ppm under temperature and pressure conditions that would provide better BZ recovery and AA retention. At last, BZ-AA-water ternary solutions at different concentrations were pervaporated in order to study the flux coupling phenomenon.

Sample analysis

The benzaldehyde concentration in the

permeate was determined by measuring the sample absorbance (λmax = 249 nm) using a UV spectrophotometer (Varian Cary 50) and quartz cuvettes. The absorbance calibration curve as a benzaldehyde concentration function was linear at 2 to 7 ppm range. Acetic acid was quantified by high-performance liquid chromatography (HPLC), based on the method employed by Zuim *et al.* (2011).

Results and discussion

The compounds assessed in the present work (benzaldehyde and acetic acid) are reported in the literature as key ones in the coffee aroma composition (Ribeiro *et al.,* 2012) since they confer different characteristics. Benzaldehyde has a bitter almond aroma, providing a pleasant aroma to the product. Acetic acid, on the other hand, is related to a penetrating and irritating odour, and is commonly associated with the vinegar odour, harming the aroma composition (Moreira *et al.,* 2000). Thus, the presence of benzaldehyde is desirable, and that of acetic acid is undesirable in the final coffee aroma. Also, the concentration of volatile compounds in coffee extracts is usually in the ppm magnitude. Cheong *et al.* (2013) analysed 62 aroma-active compounds including acetic acid in a study of Asian Arabica coffee varieties, and reported 17 to 40 ppm concentration of these compounds in a concentrated ground coffee bean extract.

These aspects ought to be considered when performing a recovery procedure for compounds that will be reincorporated during coffee or coffee-aroma products processing. Therefore, the present work aimed at establishing better conditions for benzaldehyde recovery and the acetic acid rejection in the permeate obtained from pervaporation of their binary solutions.

Membrane characterisation

Pervaporation experiments using water as feed solution were performed to verify the PDMS membrane behaviour. The temperature and pressure conditions were similar to those used for the volatile organic compounds studied. The water permeation flux exponentially increased with temperature, showing a dependency based on the Arrhenius model in Eq. 10.

The apparent activation energy (E_a) for water estimated by a non-linear regression presented 38.18 kJ/mol value, with 0.997 correlation coefficient, which is similar to those observed in pervaporation of water using PDMS membrane (Martínez *et al.,* 2013; Weschenfelder *et al.,* 2015). The results also showed that the water flux decreased with the increase of the permeate pressure, which is due to the decrease of the partial pressure gradient. Such expected behaviour has shown that water permeation flux through the membrane following the sorption-diffusion model (Eq. 7).

Binary mixture pervaporation

Temperature is an important parameter in pervaporation study since it affects all sorption-diffusion model steps, which is used to justify mass transport through the membrane (Peng *et al.,* 2003). The temperature effect on the individual benzaldehyde and acetic acid fluxes at different pressures is shown in Figure 1(A) and 1(B), respectively.

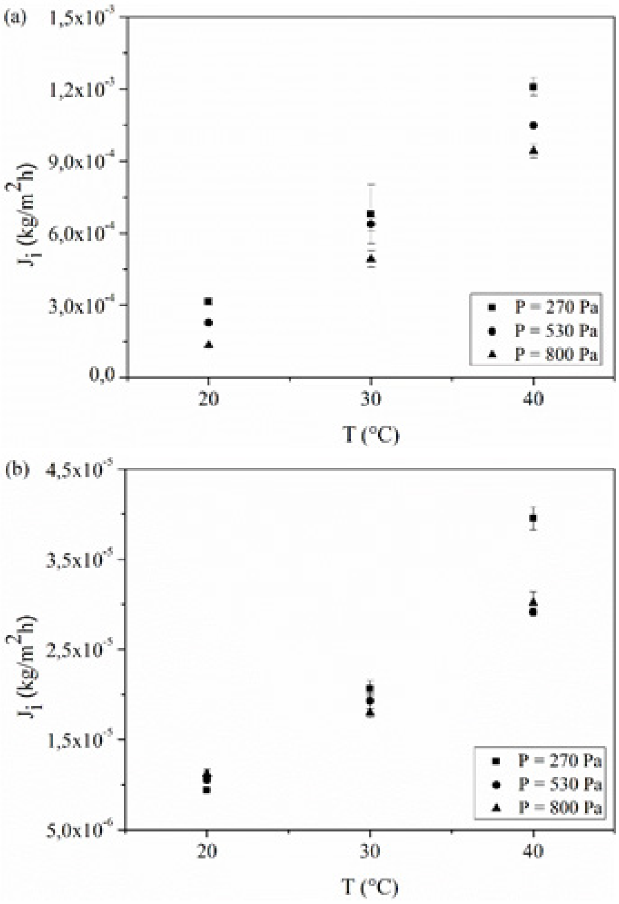

Figure 1. Feed temperature effect on individual permeation fluxes for benzaldehyde (A), and acetic acid (B).

Figure 1 displays an increase in the BZ and AA solutions individual flux with increasing feed temperature. Such behaviour is expected since based on Eq. 7, increasing the feed side component vapor pressure enhanced the driving force for permeation.

The flux dependence with temperature may also be justified in terms of polymer mobility. At higher temperature amplitude, the frequency of the polymer chain oscillations increases, resulting in a free volume rise among the polymer chains.

Subsequently, aroma molecules easily fill the created free volumes; thus, increasing the partial fluxes of organic compounds (Dawiec-Liśniewska *et al.,* 2018). The thermal motions of the penetrating molecules inside the membrane increase with the rise in temperature, favouring their diffusion.

The estimated values for apparent (E_a) and permeation (E_p) activation energies of compounds were studied, and their correlation coefficients were calculated. The correlation coefficient was at a minimum 0.935, proving that the dependence of organic compound flux of temperature is justified by the non-linear form of Arrhenius equation.

The apparent activation energies of volatile aroma compounds varied with pressure. Aroujalian and Raisi (2007) obtained similar behaviour in their study on volatile aroma compounds recovery from orange juice by pervaporation. In the present work, BZ activation energy was higher than water activation energy at all studied pressures, demonstrating that pervaporation through the membrane is more temperature-dependent than water permeation (E_a BZ = 51.33 kJ/mol and E_a water = 40.16 kJ/mol at 270 Pa; E_a BZ = 58.46 kJ/mol and E_a water = 39.74 kJ/mol at 530 Pa; E_a BZ = 74.82 kJ/mol and E_a water = 40.85 kJ/mol at 800 Pa). For acetic acid, this generalisation cannot be assumed since its E_a was smaller than E_a for water in tests performed at 530 and 800 Pa (E_a AA = 54.87, 38.93, and 37.76 kJ/mol at 270, 530, and 800 Pa, respectively). The high individual BZ flux at low pressures observed in Figure 1(A) is also justified in terms of E_a. As E_a was low at low pressures, the permeation of this compound through membrane was facilitated, resulting in a larger individual flux. On the other hand, the E_a of AA was lower than that of water at 530 and 800 Pa pressures, justifying the increase of individual flux with the increased pressure at 20°C (Figure 1(B)).

These results showed that the interaction between the compounds of the feed solution interfered with the apparent activation energy value, which is enhanced when observing the results found in the literature on pervaporation of diluted multicomponent solutions. Weschenfelder *et al.* (2015) estimated the E_a of BZ at a 34.31 kJ/mol value when studying the pervaporation of an industrial soluble coffee solution. Martínez *et al.* (2013) found the E_a of benzaldehyde at a 37.5 kJ/mol value in a synthetic multicomponent solution containing eight volatile compounds. Both works were performed using PDMS membrane.

The temperature effect on membrane permeation is justified in terms of permeation activation energy, E_p, which describes the temperature effect on membrane permeability. According to Feng and Huang (1996), E_p could be determined by subtracting the vaporisation enthalpy (ΔH_v) from the apparent activation energy calculated from the ln J vs. 1/RT plot slope, i.e., $E_p = E_a - \Delta H_v$.

E_p (kJ/mol) calculated values were -0.50, -0.92, and 0.19 for water, 8.83, 15.96, and 32.2 for benzaldehyde, and 31.51, 15.57, and 14.40 for acetic acid at 270, 530, and 800 Pa, respectively.

E_p could also be stated as the activation energy required for the permeating molecules to diffuse through the membrane (E_d), plus dissolution enthalpy (ΔH_s) for feed molecules sorpted into the membrane ($E_p = E_d + \Delta H_s$) (García *et al.,* 2009). As the temperature increases, the solubility and diffusivity of a compound decreases and increases, respectively; thus, due to exothermic sorption process, the E_d and AH_s values are positive and negative, respectively. Consequently, E_p will be positive ($E_d > \Delta H_s$) or negative ($E_d < \Delta H_s$) depending on the sorption and diffusion contribution level. Therefore, the positive value of the activation energy for BZ and AA permeation indicates that membrane permeability increased with temperature; and furthermore, temperature had a greater effect on diffusion than on the sorption of the studied compounds. These results differed from the behaviour observed by Martínez *et al.* (2013) and Weschenfelder *et al.* (2015) for PDMS membrane, who studied solutions with compounds from different chemical classes. This behaviour might have occurred due to solutions containing various organic compounds, even at low concentrations, could alter the thermodynamic behaviour of the feed solution using the pervaporation membrane. Otherwise, a coupling effect of BZ by the presence of other compounds could have occurred.

The feed temperature effect on BZ and AA enrichment factor in the binary solutions can be seen in Figure 2. Since BZ individual flux is more sensitive to changes in temperature based on the higher E_a value presented, the enrichment factor is expected to increase with temperature. This was observed in the 20 to 30°C range. On the other hand, water molecules diffusion is facilitated at higher temperatures due to its low molar volume, and increasing its flux through the membrane. Thus, the tendency for BZ enrichment factor to remain constant at both higher temperatures and pressure was observed. García *et al.* (2009) noted an increase in the compounds flux, and minor alterations in the enrichment factor with temperature.

The enrichment factor variation for AA was similar to that of BZ at 270 and 530 Pa pressure. However, a decrease in enrichment factor for AA occurred at 800 Pa, when temperature increased from

20 to 30°C, but no significant change occurred at 40°C. The high-water molecules mobility through the membrane due to its small molar volume, combined with E_a value higher than that of E_a for AA at 800 Pa, caused higher water flux. Therefore, at higher temperatures, despite the higher AA individual flux, the AA enrichment factor remained virtually constant as the water flux also increased. Moreover, AA enrichment factor was less than 1.0, indicating that its concentrations in the permeate were lower than in the feed. Enrichment factors less than 1.0 for AA in PDMS membranes were also found by Overington *et al.* (2008).

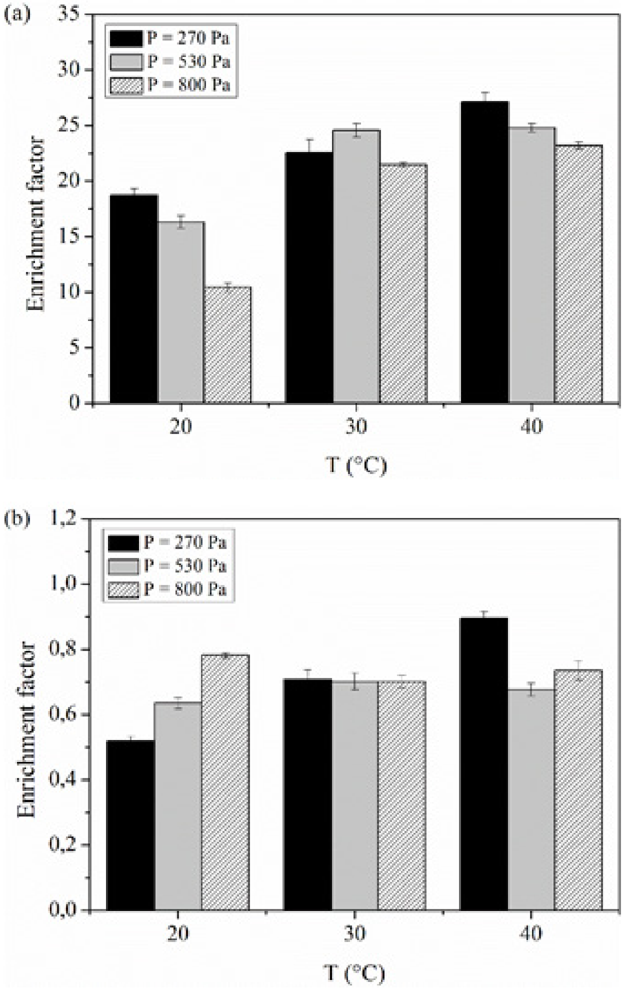

Figure 2. Feed temperature effect on binary solutions enrichment factor at different permeate pressures (feed flux rate = 3.0 L/min) for benzaldehyde (A), and acetic acid (B).

The highest individual flux and selectivity for both compounds were obtained at 40°C and 270 Pa. BZ also showed good results at both 30 and 40°C at 530 Pa for enrichment factor, yet its flux decreased when the temperature decrease. For AA, lower enrichment factor and individual flux were obtained at 20°C and 800 Pa. However, such conditions provided a similar result for benzaldehyde, resulting in their rejection. Since the membrane was more selective for BZ and the enrichment factor for AA was less than 1.0 in all conditions studied, 40°C and 270 Pa were defined for subsequent assays.

Feed concentration effect

In pervaporation, the solubility and diffusivity of feed components might be affected by the presence of another volatile compound which is called the coupling phenomenon. Coupling effects occur by the interactions between individual components and the polymeric membrane, combined with the mutual interactions among the permeants in the membrane. Thus, this part of the study was performed with BZ-water and AA-water binary solutions at 20, 40, and 60 mg/L at 40°C and 270 Pa permeate pressure. Figure 3 shows the feed concentration effect on total flux (A), organic flux (B), and enrichment factor (C).

It is observed in Figure 3(A) that the total flux using BZ-water solutions remained somewhat constant with the increased of BZ concentration in the feed, while the total flux using AA-water solutions recorded a small variation. Even so, this variation was not significant, since it occurred in the 1.08 ± 0.01 to 1.11 ± 0.01 kg/m^{2}h range. Thus, due to high dilution in feed concentration, the changes in feed concentration did not influence total flux, remaining nearly constant and close to the flux obtained when water was used as the feed solution, under the same temperature and pressure conditions (1.18 ± 0.03 kg/m^{2}h).

Figure 3(B) showed an acceptable linear dependence between the individual BZ and AA flux, and the feed concentration, thus the BZ flux increase was much greater than that noted for AA flux. This is in accordance with Eq. 9, which presents a linear function between the individual flux and feed concentration. This linear relationship indicates that membrane swelling might be negligible (Peng *et al.,* 2003).

Assuming that membrane swelling does not occur, and that the activity coefficient of compound remains constant in diluted systems, the organic compounds, water permeability, and consequently the separation factor, will remain constant (Martinéz *et al.,* 2013) as shown in Figure 3(C). Enrichment factor for BZ and AA remained virtually constant when their concentration in the feed increased.

For the compounds studied, the PDMS membrane showed greater selectivity to BZ than to AA due to the greater affinity of BZ with the polymer. At higher concentrations, the BZ flux was greater than the AA flux, reflecting higher BZ enrichment factor value. A high enrichment factor for BZ was also

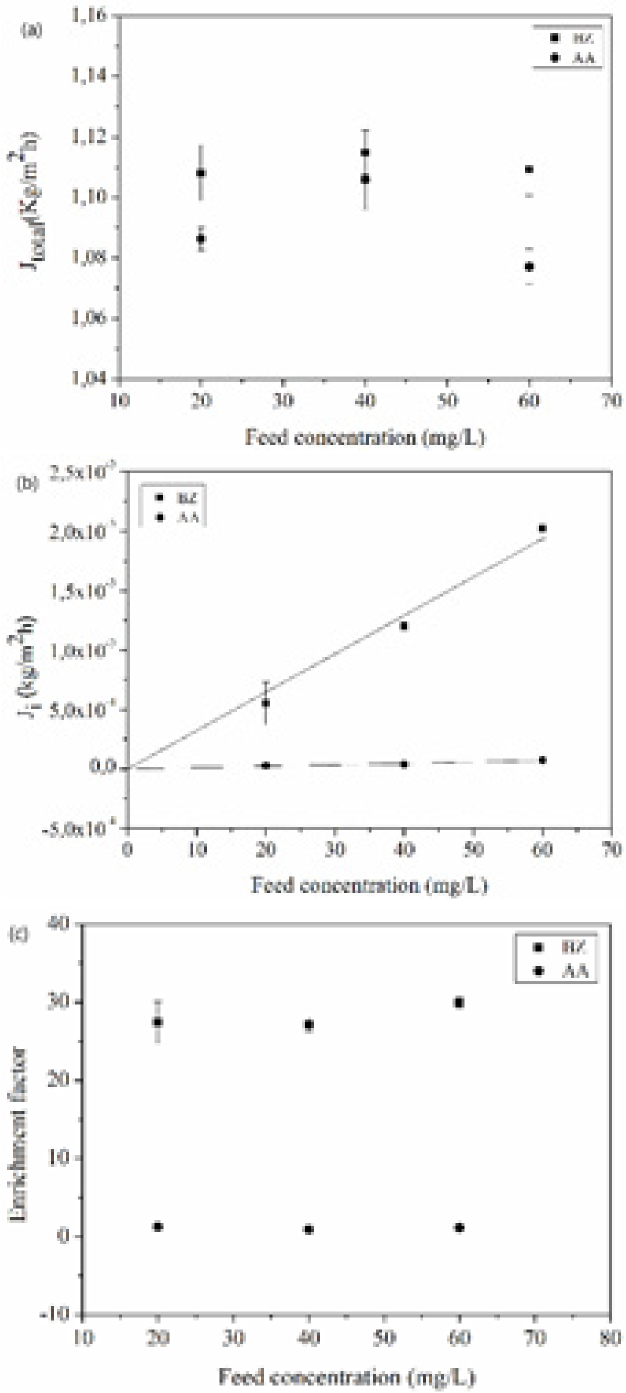

Figure 3. Feed concentration effect on (A) total flux, (B) individual permeation fluxes for benzaldehyde and acetic acid, and (C) benzaldehyde and acetic acid enrichment factor.

reported by Martinéz *et al.* (2013) when studying pervaporation of a diluted multicomponent system, obtaining a value of 51 for this parameter at 26°C and 300 Pa using a PDMS membrane.

The separation characteristics of the membrane mainly depend on sorption, whereas, diffusion determines the permeants transportation speed through the membrane. The selective sorption of permeants through the membrane is the result of their mutual solubility in the membrane, which depends on polarity. Hence, the to-be-segregated compound must have a polarity close to that of the membrane.

The penetrant-polymer interaction and the affinity between them could be analysed by comparing Hansen's solubility parameters (García *et al.,* 2009; Li and Luis, 2018). The solubility parameter is a cohesive force measure that holds molecules together in the liquid phase, as expressed by Eq. 11 (García et al., 2009):

$$\Delta\delta_{i,3} = \sqrt{[(\delta_{d,i} - \delta_{d,3})^2 + \left(\delta_{p,i} - \delta_{p,3}\right)^2 + [(\delta_{h,i} - \delta_{h,3})^2]} \qquad \text{(Eq. 8)}$$

where, δ = solubility parameter, and δ_d, δ_p, and δ_h = dispersive, polar, and hydrogen bonding contributions to the solubility process, respectively. The three partial solubility parameters for BZ, AA, water, and PDMS, together with the permeant/polymer interaction $\Delta\delta_i$,3 is listed in Table 1.

Table 1. Solubility parameters (MPa$^{0.5}$) for benzaldehyde (BZ), acetic acid (AA), water, and PDMS (Green and Perry, 2001).

Compound	δ_d	δ_p	δ_h	$\Delta\delta_{i,3}$
Benzaldehyde (BZ)	19.4	7.4	5.3	8.12
Acetic acid (AA)	14.5	8	13.5	11.91
Water	15.6	16	42.4	40.92
PDMS	15.9	0.1	4.7	

In compliance with this theory, the polymer membrane will have a higher affinity towards the permeant of which solubility parameter is similar to that of the polymer, i.e., $\Delta\delta_i$,3 value closer to zero. The permeant/polymer interaction $\Delta\delta_i$,3 was lower for BZ than for AA, confirming the higher membrane affinity for BZ than for AA.

The permeability of organic compounds through the membrane was calculated from the angular coefficients obtained from Figure 3(B), using Eq. 9, at 9.68×10^{-11} and 3.47×10^{-12} m^2/s for BZ and AA, respectively. Membrane permeability is dependent on the permeant compound properties, such as chemical structure, molecular size, hydrophobicity, activity coefficient, and equilibrium vapor pressure, as well as the interaction between the permeant and membrane material (Raisi *et al.,* 2008). The higher membrane permeability for BZ is justified in terms of chemical structure and is related to membrane morphology and the polarity/solubility of the aromatic compounds studied. Despite the hydrophilic CHO group is part of the BZ structure, the benzene ring has an enormous effect on the compound properties, making it hydrophobic (Baudot and Marin, 1997).

Thus, the hydrophobic characteristics of the membrane would indicate a greater BZ flux as compared to the AA.

Ternary mixture pervaporation

Assays were performed using ternary BZ-AA-water solutions at different concentrations in order to verify the effect of another molecule on the studied organic compounds flux. The solutions used as feed contained 20, 40, and 60 mg/L of each organic compound. The assays were carried out at 40°C and 270 Pa.

The total flux remained virtually constant for the concentration range studied, obtaining mean flux of 1.066 ± 0.013 kg/m^2h for the three solutions. A comparison between the fluxes and enrichment factors of pervaporation from both binary and ternary solutions is shown in Table 2.

In Table 2, it is apparent that the enrichment factors decreased in the ternary solutions as compared to the binary solutions in all experiments, except for AA in the 40 mg/L solutions, which presented a 4.3% increase. The most significant reduction occurred with enrichment factor for BZ in the 60 mg/L ternary solution, which decreased from 29.93 ± 0.59 to 23.27 ± 0.09 (22% drop). At lower feed concentrations, the reduction in enrichment factor for BZ and AA was virtually the same. Such reduction was more significant for BZ than for AA at the highest concentration. Table 2 also shows that membrane selectivity for BZ was on average of 25 times higher than that for AA.

The individual flux of the compounds in binary and ternary solutions was analysed to see if the flux coupling phenomenon influenced the molecules permeation. When no significant interactions occur between the two aroma compounds, the permeation flux of compounds ought to be the same as in the pervaporation case of binary mixtures involving a single compound under the same operating conditions (Isci *et al.,* 2006). However, this was not the case. As for the enrichment factor, the individual fluxes decreased in the presence of another organic molecule. BZ was more sensitive than AA to changes in the feed solution composition at all concentrations studied. The greatest reduction occurred in 60 mg/L solutions with a 25% individual flux decrease.

The calculated permeability values for the two compounds in the ternary solutions also justified the negative effect caused by other organic molecules in the feed solution. The permeability values for BZ and AA in the ternary solution were 7.67 × 10-*11* and 3.47 × 10-*12* m^2/s, respectively. This indicates that another organic compound in the feed solution may affect the membrane selectivity due to interactions among the different aroma compounds.

Further studies on organic compound multicomponent mixture pervaporation reported both positive and negative interactions among aroma compounds. Isci *et al.* (2006) observed that methyl butyrate flux was halved in a food solution containing ethyl butyrate (ETB), whereas ETB flux remained constant. On the other hand, a positive effect was noted on 1-octen-3-ol permeation by Martinéz *et al.* (2011) that presented a higher permeability in a multicomponent mixture as compared to binary system.

Conclusion

Based on the results obtained in the present work, it can be concluded that pervaporation is a

Table 2. Individual flux (J_i) and enrichment factor (*β*) comparison at different feed concentrations for benzaldehyde and acetic acid in binary (BZ-water and AA-water) and ternary (BZ-AA-water) solutions at 40°C and 270 Pa.

	Benzaldehyde		**Acetic acid**	
	BZ-water	**BZ-AA-water**	**AA-water**	**BZ-AA-water**
20 mg/L				
J_i (kg/m^2h)	6.08E-04 ± 5.5E-5	4.96E-04 ± 4.3E-6	2.69E-05 ± 2.0E-6	2.19E-05 ± 1.7E-6
β	27.44 ± 2.65	22.98 ± 0.38	1.24 ± 0.09	1.01 ± 0.09
40 mg/L				
J_i (kg/m^2h)	1.21E-3 ± 3.8E-5	1.10E-3 ± 2.9E-05	3.95E-5 ± 1.3E-6	3.93E-5 ± 1.9E-6
β	27.12 ± 0.86	26.03 ± 0.47	0.89 ± 0.02	0.93 ± 0.03
60 mg/L				
J_i (kg/m^2h)	1.99E-03 ± 4.5E-05	1.49E-03 ± 4.8E-05	7.25E-05 ± 6.3E-6	6.52E-05 ± 3.7E-6
β	29.93 ± 0.59	23.27 ± 0.09	1.12 ± 0.10	1.01 ± 0.06

promising technique for coffee volatile compound recovery and separation. All permeation fluxes increased with temperature, following an Arrhenius-type relation, where temperature has greater effects on diffusion than on sorption. Enrichment factor for benzaldehyde increased with temperature at 270 Pa, yet it remained virtually constant at 30 to 40°C range, at 530 and 800 Pa. Therefore, BZ pervaporation ought to be performed at lower pressures and higher temperatures. As the feed concentration increased, a linear individual fluxes increase of the organic compounds occurred, yet both compounds enrichment factors remained virtually constant. From the ternary BZ-AA-water system, a reduction in fluxes and in enrichment factor for both BZ and AA occurred, and such reduction was more significant at higher concentrations. This leads to the assumption that the presence of another organic molecule negatively affected pervaporation performance of both compounds. BZ was more sensitive to change in the feed solution composition in all concentrations studied.

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