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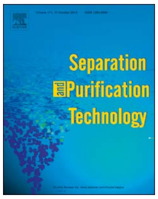

Understanding coupling effects in pervaporation of multi-component mixtures

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ABSTRACT

The application of pervaporation for the separation of multicomponent mixtures may involve coupling effects among components and the membrane, which could increase or decrease the permeance of the target compound. In order to study and describe this phenomenon, mixtures of components present in two model reactions have been considered: the transesterification reaction between methyl acetate and butanol to produce methanol and butyl acetate, and the transesterification reaction between methanol and ethyl acetate to produce ethanol and methyl acetate. Both reactions are of utmost interest in the chemical industry and present high cost of separation due to the presence of azeotropic mixtures (*i.e.,* methanol/methyl acetate; butanol/butyl acetate; ethanol/ethyl acetate).

The separation performance of four commercial membranes (*i.e.,* PERVAP 1255-30, PERVAP 4155-40, PERVAP 1255-50, PERVAP 4155-80) from Sulzer Chemtech, Switzerland, is evaluated. The effect of the feed concentration and the temperature on the separation performance was studied in terms of permeance and selectivity. Coupling effects were observed when the permeance of pure solvents was compared with that of the components in the mixture. The coupling effects were analyzed by the Hansen solubility approach and by the variation of activities within the membrane.

1. Introduction

The application of pervaporation to separate azeotropic mixtures has been studied and its technical feasibility is proved [1]. In pervaporation, the membrane is a selective barrier that determines which molecules can pass through. The feed side is liquid phase, and the permeate side is vapor phase. Vacuum is applied on the permeate side. Therefore, the driving force is the difference of the partial pressure of the component across the membrane between the feed and permeate sides. The interaction between the molecules and the membrane results in the solubility and diffusivity of the component and determines if the molecules can pass through the membrane from the feed side to the permeate side. Hence, the presence of an azeotrope has no impact on the separation due to its different separation mechanism comparing with distillation [2]. However, the separation of organic-organic mixtures by using pervaporation is still a challenge due to the lack of membranes able to separate two organic compounds. One of the reason of the poor selectivity of the membranes for organic-organic mixtures is caused by coupling effects. The transport mechanism of solution-diffusion can be considered for pervaporation, consisting of three stages: (1) the molecules are adsorbed on the membrane at the feed side, (2) the molecules diffuse through the membrane, and (3) the molecules are desorbed as vapor phase at the permeate side [3]. Therefore, the permeation can be described in terms of solubility and diffusivity. The solubility is a thermodynamic property. In multi-component mixtures, there exists an interaction which influences activity coefficients between each component and an interaction between each component and the membrane [4]. This will affect the amount of each component present in the membrane. The driving force is calculated from the activity coefficient and mole fraction of the component in the feed liquid [5]. According to the work by Binning et al. [6], the polymer film under permeation can be divided in two zones: the solution phase zone and the vapor phase zone. Selectivity in separating mixtures occurs at the two interfaces. The phase transition from liquid phase to vapor phase takes place within the polymer film. Therefore, the activity coefficient and mole fraction of the component liquid inside the membrane is different from those in the feed liquid due to the interaction between the component and membrane material. Hence, the real activity coefficients should be taken into account located at the interface of solution phase zone and vapor phase zone. As a result, the interface of a liquid phase and a vapor phase inside the membrane will affect this driving force. However, most of the recent research is assuming that the activity

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coefficients of the feed solution can be applied without taking into account the interaction between the solution and polymer. On the other hand, diffusivity is a kinetic property. When one component diffuses through the membrane faster than other components, a drag effect may happen. Fast compounds can drag slow compounds diffusing through the membrane together, leading to coupling effects. A mutual drag coefficient can be introduced to describe two coupled diffusion flows [7]. However, preferential sorption is the prerequisite to the preferential permeation [8]. Hence, the solubility factor plays an important role on the performance of pervaporation polymeric membranes. Hansen solubility parameters approach is a useful method to predict the solubility behavior of the solvent and polymers. For instance, the solubility of polymer and pure substance can be predicted by Hansen solubility parameter to select appropriate solvent. In the literature [9,10], Hansen solubility parameters have been used extensively for the interpretation the interaction and affinity between polymer and penetrants. Only data of the interaction of pure components was used and compared for the interpretation of coupling effects. Actually, the solubility of pure solvent and mixture may be quite different. The study of solubility parameter of mixture is missing. In this work, a detailed study is carried out in order to determine how the differences in solubility of a mixture and a pure substance influence the performance of pervaporation process.

The measurement of coupling effects is difficult due to coupled fluxes in which the presence of one component can affect the transport rate of the other [11]. Therefore, many studies have been carried out for binary [8] or ternary [12] systems, but the study of multicomponent mixtures with four components [13] is scarce. Research results show that coupling effects are quite different in different scenarios. For example, She et al. [14] observed no coupling effects in pervaporation of dilute flavor organics. However, Raisi et al. [15] found that coupling effects cannot be neglected when the presence of some aroma compounds has influence on the permeation of other aroma compounds. The pervaporation performance of alcohol – ester mixtures has been investigated by Luis et al. [16,17]. However, coupling effects are not systematically studied. Thus, a deeper understanding of when and how coupling effects take place in these mixture is important.

Pervaporation has been applied for organic-organic separations [18], waste water treatment [19], water separation for esterification reactions [20,21] and alcohol dehydration [22]. For equilibrium limited reactions, pervaporation membranes can be applied for the selective removal of a by-product in the reaction resulting in shifting the reaction to a higher production yield according to the principle of Le Chatelier-Braun. In addition, if azeotropic mixtures are present, pervaporation can be also applied to separate those mixtures since the separation is not based on the thermodynamic equilibrium. In this work, the following model reactions have been considered for the coupling effect study:

Reaction 1: transesterification reaction of methyl acetate and n-butanol to yield n-butyl acetate and methanol:

$$CH_3COOCH_3 + CH_3(CH_2)_3OH \leftrightarrow CH_3COO(CH_2)_3 + CH_3OH$$

Reaction 2: transesterification of ethyl acetate and methanol to produce methyl acetate and ethanol:

$$CH_3COOCH_2CH_3 + CH_3OH \leftrightarrow CH_3COOCH_3 + CH_3CH_2OH$$

These two reactions are characterized by a low conversion (chemical equilibrium constant close to unity) and the formation of two pairs of azeotropes: methyl acetate/methanol and butanol/butyl acetate in reaction 1, and methyl acetate/methanol and ethyl acetate/ethanol in reaction 2. Due to the high cost of separation by means of conventional methods such as distillation, pervaporation seems to be a more effective approach to consider.

Reaction 1 has been the focus of attention of several researchers since the product butyl acetate is an important and useful solvent for various applications, *e.g.*, paint and coating manufacture and lacquer industry, and methanol is the feedstock of poly-vinyl-alcohol. For example, Jimenez et al. [23] evaluated the recovery of a mixture of methanol and 30 wt% methyl acetate from the poly(vinyl alcohol) process. This mixture was concentrated to ~80 wt% methyl acetate and processed by reactive distillation in order to overcome the limitations of the azeotropic mixture. Using this approach leads to high purity of butyl acetate and methanol but the application of reactive distillation has no economic advantage [24].

Reaction 2 is considered as a model reaction for the development of different catalysts for transesterification reactions [25–27]. In this reaction, the product methyl acetate is one of the compounds in the production of biodiesel. In addition, this transesterification reaction contains a quaternary organic mixture with two azeotropes (methyl acetate/methanol and ethyl acetate/ethanol), thus, reactive pressure swing distillation has been proposed for breaking the azeotropes and achieving separation [28,29]. This process requires two distillation columns in which the components of the feed stream and recycle stream from the second column are separated at a specific pressure at the first column. Then, the azeotropic mixture at the bottom is separated by a second column that operates at a different pressure. This technique consumes high energy and presents high capital costs.

In this work, recommended commercial membranes for organic-organic separations from Sulzer are used at different temperatures and different concentrations of feed solutions in order to evaluate the performance of each membrane for the two model transesterification mixtures and determine the degree of separation that those membranes can offer. The objective of the work including twofold. Firstly, coupling effects are evaluated by studying and comparing the solubility of pure substances and mixtures in the polymeric membrane. Secondly, the variation of activities within the membrane was investigated.

2. Experiments

2.1. Materials

The chemicals used in the experiments were: methanol (>99%), n-butanol (>99.9%), butyl acetate (>99.7%), ethanol (>99.0%) and ethyl acetate (>99.8%), supplied by VWR PROLABO®, Belgium. Methyl acetate (>99.0%) was supplied by Merck, Germany.

2.2. Membranes

The membranes were supplied by Sulzer Chemtech (Switzerland). The types of membranes were PERVAP 1255-30, PERVAP 4155-40, PERVAP 1255-50 and PERVAP 4155-80. The membranes are composed of three layers. The active layer of the membranes contains polyvinyl alcohol (PVA) with a thickness of 0.5–5 µm layer. A porous support layer containing polyacrylonitrile with a thickness of 70–100 µm in the middle, and the mechanical support layer contains polyphenylene sulfide with a thickness of 100–150 µm at the bottom. In sorption test, this mechanical support layer (polyphenylene sulfide) was removed.

2.3. Gas chromatography analysis

A gas chromatograph (Shimadzu GC-14A) is applied for the analysis of composition of permeate and feed solution. The mobile phase is Helium. The packed column is Stabilwax (Length: 30 m, Internal Diameter: 0.32 mm, DF: 1.0 µm) and equipped with FID (flame ionisation detector). The initial inject temperature is 200 °C and the detector temperature is 250 °C. The parameters of the headspace (injection of vapor) are: the temperature is 80 °C, the temperature of the needle is 100 °C, the thermostatisation time is 15 and 30 min and the injection time is 0.02 min. The molar fractions of the organic compounds based on a calibration curve were obtained from the analysis of the gas chromatograph.

2.4. Pervaporation experiments

Pervaporation experiments were carried out using the pervaporation laboratory test unit 3″ round cell from Sulzer Chemtech, Switzerland. Two different quaternary mixtures were prepared as feed solutions: (1) methyl acetate, n-butanol, butyl acetate and methanol, named mixture M1; and (2) ethyl acetate, methanol, methyl acetate and ethanol, named mixture M2. Both mixtures were stored in a 1.5-liter stainless steel feed tank. The selection of concentration in the feed was based on the work by Jimenez et al. [23], in which the feed mole fraction of the mixture M1 is: 0.2 (methyl acetate), 0.15 (n-butyl acetate), 0.35 (methanol) and 0.3 (n-butanol). For mixture M2, in the work of Dossin et al. [27], the molar ratio of methanol/ethyl acetate is 0.1–10. In order to make a comparison with the mixture M1, the same organic solvents keep the same molar fraction in the mixture M2. Therefore, the concentration of methyl acetate and methanol is kept the same as those in M1. The mole fraction of ethyl acetate and ethanol is 0.15 and 0.3, respectively. In this work, each experiment was carried out twice in order to check the reproducibility of experimental results.

Feed solutions of the pure components were prepared as well. The experimental temperature (temperature in the membrane cell) was kept at 30, 40 and 50 °C. A heating circulator (Julabo model ME, Germany) was used to maintain the desired operational temperature. The vacuum pressure at the permeate side is 8–12 mbar provided by a vacuum pump. A flat sheet membrane with an inner diameter of 7.0 cm (active area of 38.48 cm^2) was installed in the membrane cell. The membrane was immersed in the feed solution for 24 h before the experiment was carried out. The permeate was collected every 30 min or 60 min, depending on the amount of permeate collected. The feed sample was collected and analyzed at the beginning of the experiment and every 2 h. A constant value of feed concentration was observed, which indicates that no chemical reaction took place during the experiment and pseudo steady state could be kept due to the recycling of the retentate. The analysis of concentration was performed by a Shimadzu GC-14A gas chromatograph as indicated in Section 2.3.

During the experiment, the transmembrane flux is determined by weighing the mass of permeate over time by using a balance with precision of 10^{-4} g (Mettler-Toledo, AE200, Belgium). The transmembrane flux J ($\text{kg/m}^2\,\text{h}$) was determined by the following equation:

$$J = \frac{w}{\Delta t \times A} \tag{1}$$

where A is the membrane active surface area (m^2), Δt is the collecting time (h) and w is the weight of permeate (kg).

The experimental flux for each component (J_i) can be determined by following equation [16]:

$$J_i = J \times y_i \times \frac{m_i}{m_t} \tag{2}$$

where m_i and m_t are molecular weight of the component i and the molecular weight of mixture of permeate. y_i is the molar fraction component i in the permeate side.

The molar flux for each component ($\text{m}^3/\text{m}^2\text{h}$) is calculated by the following equation:

$$j_i = \frac{J_i \times v_i^G}{m_i} \tag{3}$$

where v_i^G is the molar volume of gas i (22.4 L(STP)/mol).

Then, the permeance, $\frac{P_i}{l}$, can be calculated as follows:

$$\frac{P_i}{l} = \frac{j_i}{(x_i \times \gamma_i \times P_i^0 - y_i \times P_p)} \tag{4}$$

In this equation, the permeance is calculated by dividing the molar flux by the driving force. Therefore, the impact of driving force is removed. The permeance is expressed in GPU ($1\ \text{GPU} = 1 \times 10^{-6}\ \text{cm}^3(\text{STP})/(\text{cm}^2\text{s cm Hg}) = 7.5005 \times 10^{-12}\ \text{m s}^{-1}\ \text{Pa}^{-1}$).

The activity coefficient of each component γ_i and the vapor pressure P_i^0 are calculated by Aspen Plus with UNIFAC thermodynamic method, commonly used to predict the activity coefficient of non-electrolyte and non-ideal mixtures. The total pressure of the permeate side P_p is determined experimentally during the experiment.

The separation factor $\beta_{i/j}$ is defined as the ratio between the molar concentration of each component (i, j) in the permeate (y_i, y_j) and feed (x_i, x_j) solutions:

$$\beta_{i/j} = \frac{y_i/y_j}{x_i/x_j} \tag{5}$$

The selectivity $\alpha_{i/j}$ of the membrane is given by the ratio of permeances (or permeabilities):

$$\alpha_{i/j} = \frac{P_i/l}{P_j/l} = \frac{P_i}{P_j} \tag{6}$$

If the value of $\alpha_{i/j}$ is large than 1, it indicates that the membrane is more preferential to permeate component i than component j [17].

The temperature dependency of the permeance was calculated by using the following Arrhenius-based equation [16]:

$$\frac{P_i}{l} = \frac{P_{i,\infty}}{l} \times \exp\left(-\frac{1000 \times E_a}{RT}\right) \tag{7}$$

where P_i/l is the permeance of the component i, $P_{i,\infty}/l$ is the pre-exponential factor of permeance and E_a is the activation energy. The effect of temperature on permeance is estimated in terms of activation energy.

2.5. Sorption experiments

Sorption experiments were carried out by weighing the membranes before and after immersion into the mixtures for 7 days in order to achieve sorption equilibrium. The excess of liquid was removed from the membrane surface by using a tissue, then the membrane was weighed on a balance (Mettler-Toledo, AE200, Belgium with precision ±0.0001 g). In this work, three groups of samples were tested. The sorption degree, SD, of the membrane is calculated by the following equation [30]:

$$SD = \frac{m_w - m_d}{m_d} \times 100\% \tag{8}$$

where is the mass of membrane (g); subscripts w and d refer to after sorption (wet) and before sorption (dry), respectively.

3. Theory

3.1. Hansen solubility theory

In order to describe coupling effects, the Hansen solubility theory is considered in this work. Hansen [31] proposed an approach based on solubility parameters to predict the solubility of components into a polymer. The basis of the approach is to introduce three main parameters: a dispersion component, a polar component and a hydrogen bonding component, leading to a three dimensional space that is represented by a sphere. The center of the sphere is determined by the Hansen solubility parameters of the polymer and the radius of the sphere is called interaction radius, which is typically determined experimentally and reported in the literature [32]. In this way, a spherical solubility region is developed in the three dimensional space. A polymer may be soluble in a solvent or blend solvent (mixture) if the Hansen solubility parameters of the solvent are located inside the polymer solubility sphere. The distance of the pure solvent or a mixture of solvents from the center of the polymer solubility sphere is calculated by following equation [32]:

$$R_a = [4(\delta_{Ds} - \delta_{Dp})^2 + (\delta_{Ps} - \delta_{Pp})^2 + (\delta_{Hs} - \delta_{Hp})^2]^{1/2} \tag{9}$$

where R_a is the distance between the solvent and the center of polymer solubility sphere ($MPa^{1/2}$), and δ refers to the Hansen solubility parameters. The first subscript, D, P and H, refer to the Hansen component: dispersion component, polar component and hydrogen bonding component, respectively; the second subscript, s and p, refer to the solvent and polymer, respectively. The difference of solubility parameters $\Delta\delta_{(s-p)}$ should be smaller than the interaction radius of polymer (R_0), then the solute could be dissolved in this polymer. The interaction radius of polyvinyl alcohol is 10.9, calculated from the Hansen solubility parameters shown in Table 2.

For liquids, the change of Hansen solubility parameters due to the temperature effect can be calculated by the Eqs. (10)–(12) [32]:

$$\frac{d\delta_D}{dT} = -1.25\cdot\alpha\cdot\delta_D \tag{10}$$

$$\frac{d\delta_P}{dT} = -0.5\cdot\alpha\cdot\delta_P \tag{11}$$

$$\frac{d\delta_H}{dT} = -\delta_H\cdot(1.22\times10^{-3} + 0.5\cdot\alpha) \tag{12}$$

where α is the coefficient of thermal expansion (°C^{-1}).

The Hansen solubility parameters of the blended solvents were estimated by Eq. (13), suggested by Barton et al. [33] for calculating Hildebrand solubility parameters:

$$\overline{\delta_k} = \sum_i \phi_i\delta_{ki} \tag{13}$$

the subscripts k indicates the D, P and H Hansen components (dispersion component, polar component and hydrogen bonding component, respectively). ϕ_i is the volume fraction of different pure solvents in the mixture.

The value of solubility parameters at 30 °C of each component is shown in Table 2 based on raw data from literature [32]. For 40 °C and 50 °C, the calculated Hansen solubility parameters of pure and mixtures at different temperatures are included as Supporting Information (Tables S1 and S2, respectively).

3.2. Flory-Huggings solution theory

The difference of the activity of the components within the membrane has a contribution in causing coupling effects [4]. Flory-Huggins solution theory can be used to estimate the interaction between liquid-liquid and liquid-membrane. Since the mixture is a quaternary system, indices 1–4 indicates four components in the mixture and 5 indicates the membrane-polymer (PVA). The Flory- Huggins theory has been extended to multiple components. The Gibbs free energy of mixing as follows [34]:

$$\frac{\Delta G}{RT} = \left(\sum_i \frac{\Phi_i}{m_i}\ln\Phi_i + \sum_i\sum_{j<i}\chi_{ij}\Phi_i\Phi_j\right)\sum_i n_i m_i \tag{14}$$

The activity coefficient of a component can be derived as:

$$\ln\gamma_i = \ln\frac{\Phi_i}{x_i} + 1 - m_i\left(\sum_{j=1}^{n}\frac{\Phi_j}{\mathrm{m}_j} - \sum_{j=1}^{n}\Phi_j\chi_{ij} + \sum_{j=1}^{n}\sum_{k>j}^{n}\chi_{jk}\Phi_i\Phi_j\right) \tag{15}$$

where i refers to 5 components, x_i is the mole fraction of each component. m_i is the characteristic size of component i, which is related to the degree of polymerization. ϕ_1–ϕ_5 is the mole fractions on a segment basis, it is calculated by:

$$\Phi_i = \frac{w_i v_i}{\sum_j w_j v_j} \tag{16}$$

where v is specific volume (m^3/kg) and w is mass fraction.

Therefore, the activity can be calculated as:

$$\alpha_i = x_i\gamma_i \tag{17}$$

The above equations show that the activity of a component within the membrane is affected by the interaction between each component and the component-membrane material.

For the binary interaction between solvents, the interaction parameter χ_{ij} is strongly temperature dependent and it can be calculated by [8]

$$\chi_{ij} = \frac{1}{x_i\upsilon_j}\left[x_i\ln\frac{x_i}{\upsilon_i} + x_j\ln\frac{x_j}{\upsilon_j} + \frac{\Delta G^E}{RT}\right] \tag{18}$$

where x is mole fraction of component in the binary phase, υ is volume fraction of the component in the binary phase, ΔG^E is the excess free energy of binary mixing (J/mol).

4. Results

4.1. Sorption experiments

Table 1 shows the sorption experimental data, which is the average of three samples, and the standard deviation. An increase of the membrane weight after immersion in pure solution and in the different mixtures is observed. For pure solution, the membranes sorb preferentially more alcohols than esters with butyl acetate as exception. The sorption degree follows: butanol > butyl acetate > ethanol > methanol > methyl acetate ≈ ethyl acetate. Methyl acetate and ethyl acetate have very low sorption degree. Comparing the two mixtures, M1 leads to larger weight increase than the mixture M2. This could be caused by the presence of butyl acetate in the mixture 1. In pervaporation, when the polymeric membranes swell, the swelling of polymers involves either mutual solution of miscible substances, *e.g.* the penetrants and the polymer, or solution of the low molecular penetrants in the polymer. The affinity between the penetrant and the polymer determines the concentration of penetrant in the polymeric membrane. In either case, a higher solubility of the penetrants in the polymeric membrane leads to an enhanced chain mobility which increases the

Table 1
Sorption degree after immersion of membranes in the pure solution, in the mixture of methyl acetate, butyl acetate, butanol and methanol with molar fraction 0.2/0.15/0.3/0.35 (mixture M1), and mixture of methyl acetate, ethyl acetate, ethanol and methanol with molar fraction 0.2/0.15/0.3/0.35 (mixture M2).

Chemicals	Membrane type			
	1255-30	4155-40	1255-50	4155-80
Methanol	15.95% ± 5.6%	17.13% ± 4.5%	17.43% ± 5.2%	15.85% ± 6.1%
Ethanol	27.50% ± 4.4%	22.20% ± 5.5%	22.30% ± 6.5%	19.82% ± 5.1%
Butanol	44.69% ± 5.1%	45.58% ± 5.6%	41.81% ± 5.2%	41.72% ± 4.8%
Methyl acetate	4.17% ± 5.5%	4.78% ± 4.6%	3.80% ± 4.9%	3.97% ± 5.2%
Butyl acetate	27.90% ± 5.6%	30.21% ± 5.5%	26.71% ± 5.3%	24.46% ± 5.1%
Ethyl acetate	3.73% ± 4.9%	3.43% ± 5.2%	3.57% ± 4.7%	2.96% ± 4.8%
Mixture 1	36.47% ± 5.1%	33.98% ± 5.3%	35.75% ± 4.8%	40.51% ± 5.1%
Mixture 2	27.74% ± 5.2%	28.99% ± 5.6%	27.87% ± 5.8%	36.04% ± 5.3%

Table 2
Calculated Hansen solubility parameters of each component/mixture and R_a at 30 °C.

Material	δ_D	δ_P	δ_H	R_a
PVA	17.2	13.6	15.4	
Methyl acetate	14.1	6.9	7.3	12.1
Butyl acetate	14.7	3.6	6.1	14.5
Ethyl acetate	14.4	5.1	6.9	13.2
Methanol	15.0	12.3	22.2	8.2
Butanol	15.9	5.7	15.7	8.3
Ethanol	15.7	8.8	19.3	6.9
M1	15.1	6.6	12.8	8.5
M2	14.8	8.2	14.0	7.3

diffusivity of penetrant [35]. On the other hand, a more swollen polymeric membrane can permit a relatively large molecules diffuse through [36]. Therefore, the transmembrane flux can increase due to the swelling effect. Contrarily, the membrane selectivity can decrease because larger molecules can pass through the membrane. For this reason, it is important to be aware of the impact of swelling effects caused by the interaction between the penetrant and the polymer [37]. The sorption of penetrants by polymer is caused by the equilibrium between the chemical potentials of the penetrants in the system [38]. Therefore, it is important to immerse the membranes in the feed solution prior to perform the experiment.

4.2. Preferential permeability of pure solution

During the pervaporation experiments, the experiments of pure solution and mixture were performed twice. The transmembrane flux is the average of both experiments. The reproducibility of the results is calculated in terms of standard deviation. In order to detect coupling effects in multicomponent mixtures, it is necessary to determine the permeance of each compound when they are alone in the feed. The results of the transmembrane flux of each pure compound through the studied membranes at different temperatures are shown in Fig. S1 in supporting information. The driving force for mass transport is strongly affected by the concentration and the vapor pressure of the compound [39]. As a result, transmembrane flux cannot reflect the real interaction/affinity between compounds and the membrane material. Thus, the permeance is key to eliminate the influence of the applied driving force, shown in Fig. 1. For pure solution, the selectivity has been calculated as the ratio of the permeance of each pure compound related to the permeance of methanol.

In Fig. 1, it can be observed that all the membranes can permeate the alcohols and follow the preferential permeability sequence of butanol, methanol, and ethanol at different temperatures. The membrane 4155-40 can permeate butyl acetate only at higher experimental temperature (334 GPU at 50 °C) and the membranes 1255-50 and 4155-80 do not permeate methyl acetate, ethyl acetate and butyl acetate (permeate was not produced during the experiment). From the experimental evaluation of sorption of alcohols shown in Section 2.3, it was observed that the membranes can sorb all alcohols, which is in good agreement with the pervaporation results (all the alcohols can be permeated). Methanol has the highest transmembrane flux due to its high vapor pressure and small molecule size (Fig. S1). However, when looking at permeance in Fig. 1 to remove the effect of the driving force, it is clear that butanol has the highest permeance, followed by methanol and ethanol. In addition, the membranes 1255-50 and 4155-80 are very selective to alcohols and do not allow the permeance of esters. This result is also consistent with the result obtained from sorption of pure solutions of methyl acetate and ethyl acetate due to the low sorption degree. But butyl acetate does not follow this trend. These membranes preferentially sorb butyl acetate but no permeate was obtained. This phenomenon confronts the pervaporation results with the sorption results. The explanation could be related to the membrane-solvent interaction and the membrane structure. The membranes 4155-80 and 1255-50 could have less free volume for permeation comparing with the other two types of membranes because only certain size of molecules can diffuse easily through the membrane. According to the solution-diffusion model, the permeants have to be sorbed by the polymeric membrane, then diffuse through the membrane due to the difference of partial pressure across the membrane [8]. Therefore, after sorption, if the free volume is large as may be in the membrane 1255-30, larger molecular size compounds (such as butyl acetate, which has largest molecular size among all compounds) can diffuse through the membrane. On the contrary, when the free volume is small, the large molecules cannot diffuse through the membrane, as happens in the membranes 1255-50 and 4155-80, in which only alcohols can diffuse due to their small molecular size. On the other hand, the mobility of polymer chains and the free volume can allow faster diffusion by increasing temperature. Therefore, butyl acetate was not observed in the permeate of the membrane1255-40 at 30 °C but it was observed at 50 °C. In addition, the permeance of butyl acetate is much lower than that of methanol and ethanol, but it has higher sorption degree than these two alcohols. Thus, diffusion is the limiting factor of the permeance of this compound through the membrane.

4.3. Coupling effect in multicomponent mixtures

4.3.1. Effect of the feed composition

The experimental results of permeance and selectivity for the mixtures M1 and M2 are shown in Figs. 2 and 3, respectively. The results of transmembrane flux and separation factor for the mixtures M1 and M2 have been included in Figs. S2 and S3, respectively, as Supporting Information. The experimental data show a significant decrease in the permeance of the components when the temperature increases. This phenomena can be interpreted in terms of activation energy. The activation energy of permeation has an impact on the change of the permeation behavior of membranes caused by temperature variation [17,40]. The activation energy of diffusion is normally positive: a higher temperature enhances the diffusivity of molecules, increasing the permeation. On the other hand, the heat of solution can be negative in sorption process: higher temperature may cause disadvantage for sorption. The final activation energy of permeation is defined as the contribution of these two processes. If the sorption is dominated, the activation energy is negative, leading to a decrease of permeance with an increase of temperature.

For the mixture M1 (Fig. 2), several interesting observations can be inferred from the results. Firstly, butanol presents the largest permeance in spite of the highest flux of methanol (Fig. S2 in Supporting Information). This aspect is directly related to the effect of the higher driving force that methanol has in the mixture due to a higher volatility, as indicated before. Secondly, butyl acetate presents a permeance higher than methanol in all the membranes, while a lower permeance was observed when working with pure feed solutions. A clear coupling effect of butyl acetate by the presence of other compounds is taking place. Thirdly, methyl acetate and ethyl acetate were obtained in the permeate for the membranes 1255-50 and 4155-80 when the feed solution is a multicomponent mixture, but in Section 4.2, it was observed that both components did not permeate through the membrane regardless the temperature and only alcohols did permeate through these membranes when pure solutions were considered. This result is also an indication of the presence of coupling effects among components, in which some compounds are dragging others through the membrane.

Regarding the mixture M2 (Fig. 3), the main aspect to highlight is the dramatic increase of the permeance of ethanol when present in the multicomponent mixture. In Fig. 1, the permeance results of the pure compound showed a much lower permeance in comparison with methanol for all the membranes. However, in the mixture, ethanol is the main permeant for the membranes 1255-30 and 4155-40, it shows a similar permeance than methanol in the membrane 1255-50, and it

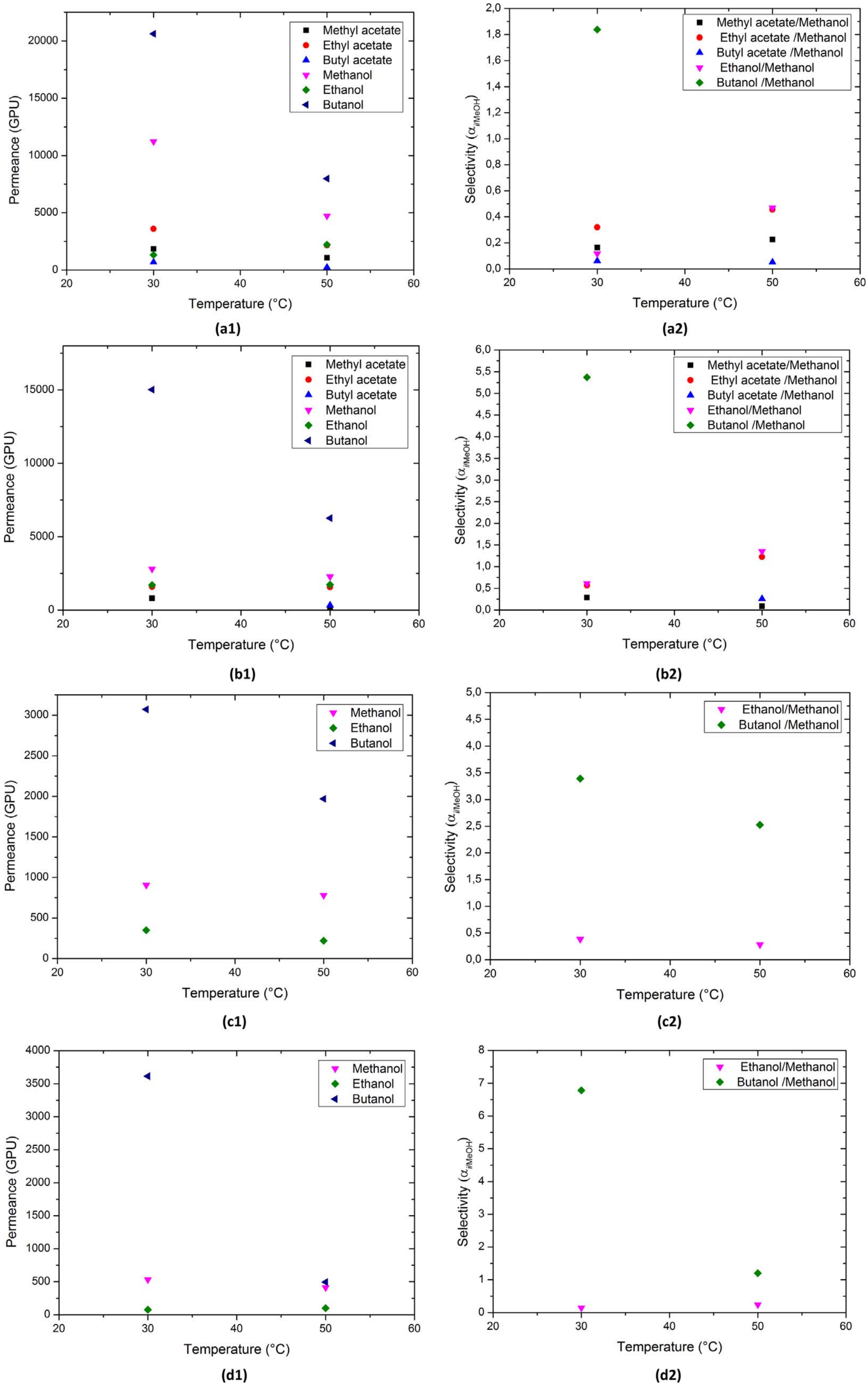

Fig. 1. The permeance (left) and selectivity of different type of membranes for different pure compounds at different temperature, (a) 1255-30 membrane, (b) 4155-40 membrane, (c) 1255-50 membrane and (d) 4155-80 membrane.

shows a slightly lower permeance than methanol in the membrane 4155-80; but in all cases, the permeance of ethanol in absolute values is increased in comparison with the results using pure ethanol as feed solution. The presence of other compounds is clearly enhancing the permeance of ethanol through the four studied membranes.

The coupling effects indicated above can be interpreted in terms of the Hansen solubility theory, described in Section 3.1. A 3D representation of the Hansen solubility sphere and projection into hydrogen-polar plane and hydrogen-dispersion plane for 30 °C are shown in Fig. 4. The 3D representation for 40 °C and 50 °C can be found as

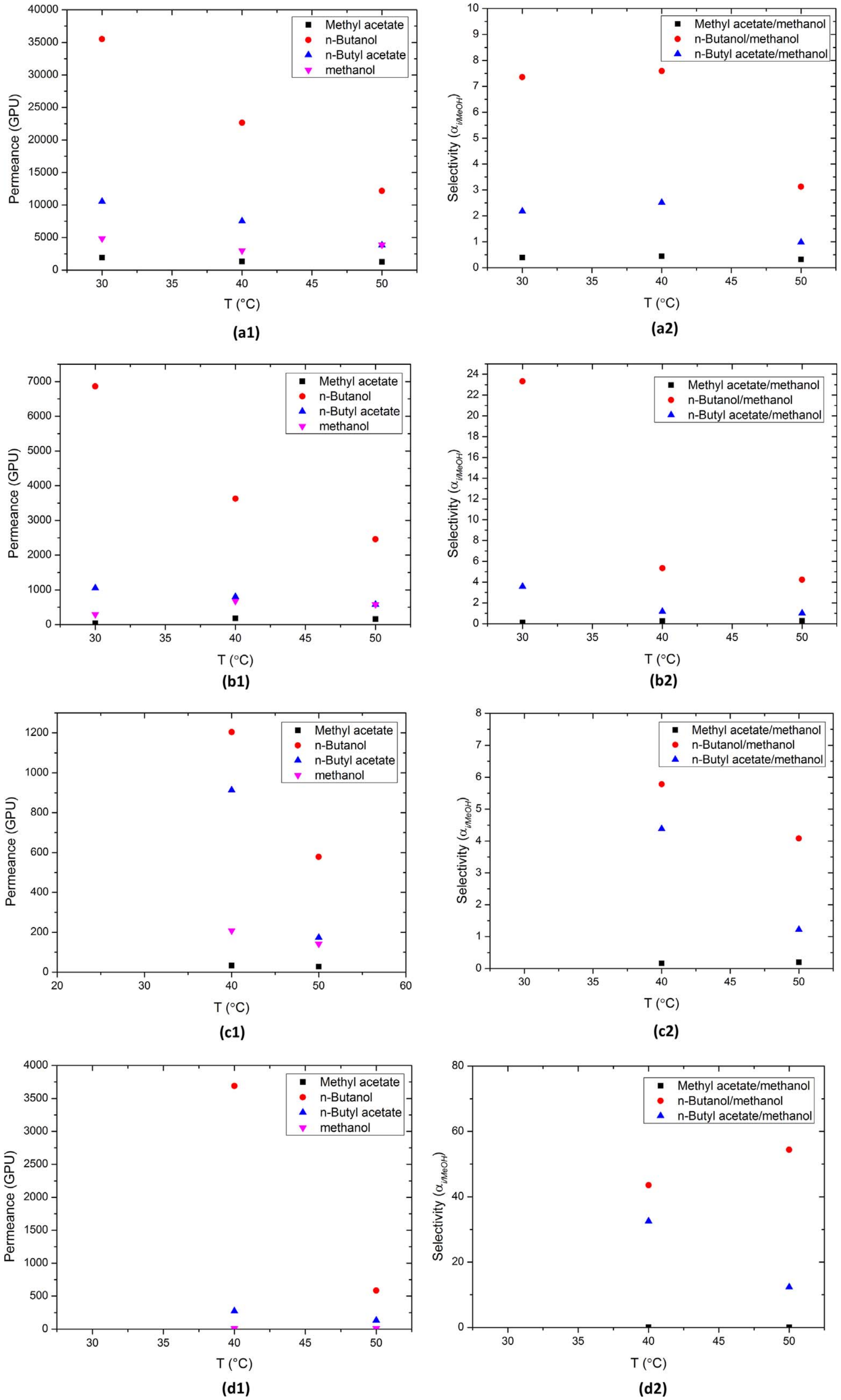

Fig. 2. The permeance (left) and selectivity (right) of different types of membranes for M1 at different temperature (a) 1255-30 membrane, (b) 4155-40 membrane, (c) 1255-50 membrane and (d) 4155-80 membrane.

Supporting Information (Figs. S6 and S7, respectively). From the information obtained from the supplier, the active layer of the studied membranes contains polyvinyl alcohol (PVA). The membrane 4155-80 contains more PVA than the other membranes, followed by 1255-50, 4155-40 and 1255-30. According to the literature [32], the interaction radius (R_0) of PVA is around 10.9. From Table 2, it is clearly shown that the distance between alcohols to the center of polymer (PVA) solubility sphere is shorter than interaction radius, therefore, these alcohols are located in the polymer (PVA) solubility sphere. On the other hand, esters were located outside of polymer (PVA) solubility sphere. This

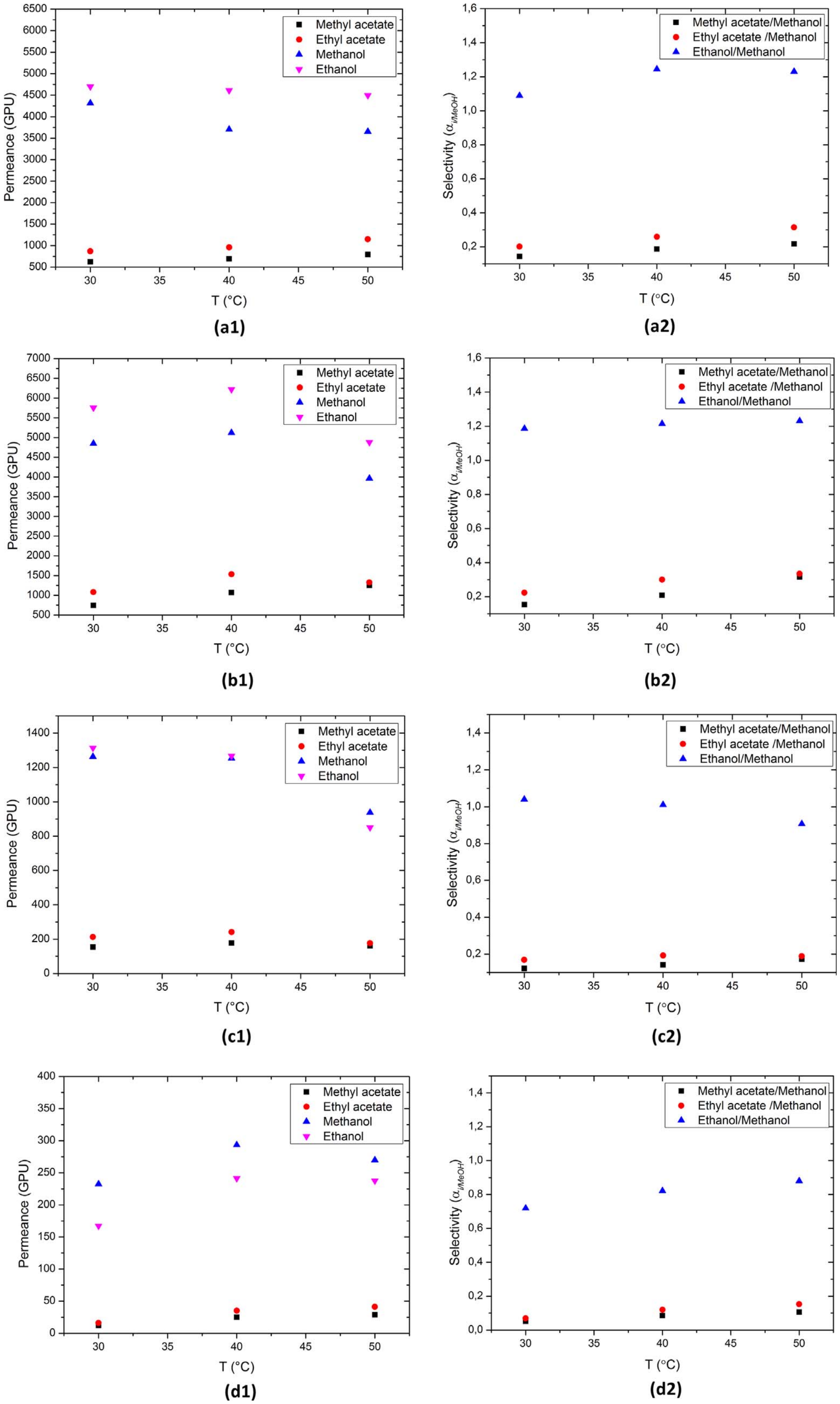

Fig. 3. The permeance (left) and selectivity (right) of different types of membranes for the mixture 2 at different temperatures (a) 1255-30 membrane, (b) 4155-40 membrane, (c) 1255-50 membrane and (d) 4155-80 membrane.

suggests that the membrane has more affinity to alcohol than esters. This could explain the phenomena observed in the sorption test, in which methyl acetate and ethyl acetate have very low sorption degree (see Table 1). In the pervaporation experiments of pure feed solution, the membranes 1255-50 and 4155-80 rejected methyl acetate and ethyl acetate because these membranes contain high fraction of PVA. These two compounds are not able to dissolve into the PVA membrane. The temperature effect can be compared with the three tables (Tables 2, Tables S1 and S2 at 30 °C, 40 °C and 50 °C, respectively.). It is observed that the solubility parameters (δ_D, δ_P and δ_H) decreased with an increase

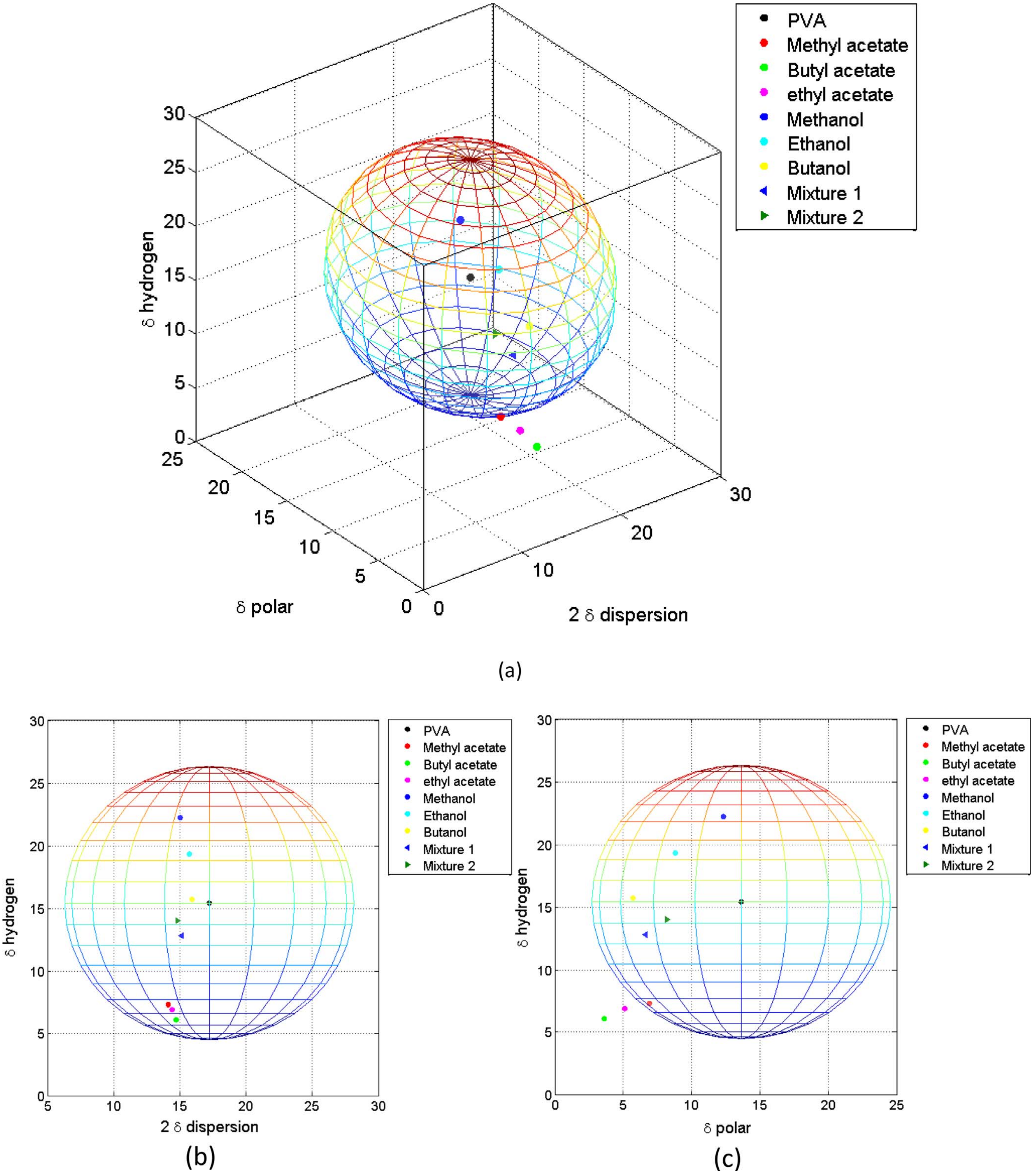

Fig. 4. Hansen solubility sphere for PVA and pure components and mixtures at 30 °C (a) 3D representation; (b) Projection into the hydrogen-polar plane and (c) Projection into the hydrogen-dispersion plane.

in temperature. But the R_a of all esters and PVA increases significantly, this also indicates that the increase of temperature does not enhance the solubility of esters to PVA.

Regarding the mixtures, the Hansen solubility parameters were changed according to the volume fraction of each component, calculated by Eq. (9). In Table 2 and Fig. 4, it can be observed that the distance between mixture M1 and mixture M2 and the PVA sphere center is 8.5 and 7.3, respectively. Both of them are located inside PVA solubility sphere. This indicates that both mixtures can dissolve in the PVA polymer. Consequently, all the components in the mixture can be sorbed by the membrane and then, diffuse through the membrane. Hence, it can be concluded that the sorption behavior of the polymeric membrane material changes due to the change of feed composition, which leads to the variation of the solubility of the different components into the polymer.

Table 3
The activity of the mixture in the feed solution and the mixture within the membrane.

Mixture 1	**Methanol**	**Methyl acetate**	**Butanol**	**Butyl acetate**
Activity within membrane (30 °C)	0.607	0.275	0.099	0.056
Activity in mixture (30 °C)	0.505	0.335	0.251	0.237
Activity within membrane (50 °C)	0.601	0.249	0.126	0.059
Activity in mixture (50 °C)	0.357	0.309	0.312	0.329
Mixture 2	**Methanol**	**Methyl acetate**	**Ethanol**	**Ethyl acetate**
Activity within membrane (30 °C)	0.611	0.221	0.288	0.114
Activity in mixture (30 °C)	0.396	0.358	0.327	0.279
Activity within membrane (50 °C)	0.566	0.232	0.313	0.129
Activity in mixture (50 °C)	0.401	0.353	0.319	0.266

4.3.2. Effect of variation of the activity coefficient within the membrane

In addition to the coupling effects caused by the different solubilities of components into the membrane, which is affected by the concentration, another aspect that can affect the permeance of components is the variation of the activity coefficient of the components within the membrane [4]. The interaction of permeants inside the membrane and the interaction of permeants and polymeric membrane in pervaporation process may have a strong impact on the performance of a polymeric membrane. The activity coefficient of one component can change when introducing other components or by contacting membrane materials. Thus, a positive or negative influence can occur on the membrane performance. In this part, only the interaction of the feed compounds and the PVA polymer material are investigated, regardless of other factors such as polymer membrane structure. The experimental data of the membrane 1255-30 is applied in the analysis as example. In order to study the thermodynamic property inside the membrane by means of activity during the pervaporation process, it is assumed that the composition within the membrane is identical to the composition of permeate. The activities of the mixture in the feed solution and the mixture within the membrane were calculated according to Eq. (17) and they are shown in Table 3 for both mixtures M1 and M2.

In Table 3, the activity of each component within the membrane and in the mixture were calculated. In both mixtures, the activity of methanol was enhanced inside the membrane. This indicates that the local driving force within the membrane can be enhanced or reduced due to the interaction between permeants and polymer. One interesting observation is obtained when comparing the separation factor of the membrane 1255-30 for both mixtures. A high separation factor indicates that the component is concentrated in the permeate. It is observed that separation factor in the mixture M1 (Fig. S3) based on butyl acetate follows: methanol > methyl acetate > butanol > 1 and the separation factor in the mixture M2 (Fig. S5) based on ethyl acetate follows: methanol > ethanol > methyl acetate > 1. These trends follow exactly the order of activity values within the membrane, although the activity of methyl acetate in the solution is higher than that of ethanol (gray color in Table 3).

The results discussed above illustrate that the coupling effect can be also explained by the activity of the component within the membrane, leading to a different driving force than that produced by the feed solution. It indicates that interaction of components and membrane material is an important factor that can influence the permeation flux and composition in the permeate due to the activity variation within the membrane. In addition, the interaction between components and the membrane material as well as the sorption capability and sorption preference to certain components by the membrane material are critical factors in determining coupling effects as indicated in Section 4.3.1.

There are some different findings in the application of commercial membranes on these two mixtures. The available information of the commercial membranes is that the membranes could contain less free volume with increasing of its series number (30 to 80). 4155-80 membrane can be a higher cross-link loading among these commercial membranes. Most surprisingly, in the mixture butyl acetate/methyl acetate/butanol/methanol, the experimental result shows that butanol is more favourable to permeate through the membrane. This finding was unexpected. The sorption of a solute in PVA depends on its polarity and molecular size. In the case of alcohols, polarity decreases with an increase in carbon number and methanol is more polar than another components. On the other hand, the chemical structure of alcohols contains −OH group, and esters contain =O and −O− group. PVA is a hydrophilic polymer with −OH group. Therefore, from the chemical structure, molecular size, hydrophilicity, PVA should more favourable to permeate methanol. In the work of Okuno et al. [41], it is found that the permeability and selectivity of PVC membrane was affected by the molecular size of alcohols, small molecular alcohol gives a high permeation. Therefore, methanol should be more favorable to permeate through the membrane due to its small molecular size. In the literature [16,17], the performance of the membranes Pervap 2250-50 and Pervap 1201 made by SULZER with a mixture of methanol/butyl acetate and methyl acetate/methanol/butanol/butyl acetate has been reported and a similar phenomenon was observed. As butanol and butyl acetate have a high sorption degree in these commercial membranes, this observation indicates that the pervaporation performance of this separation system is found to be determined by the sorption characteristics and complied with the preferential sorption is the prerequisite to the preferential permeation [8].

On the other hand, in the mixture ethyl acetate/methyl acetate/ethanol/methanol mixture, a quite different phenomenon was observed. The PVA membrane shows a better affinity to alcohols (methanol and ethanol) than esters (ethyl acetate and methyl acetate). However methanol and ethanol does not show good separation because their selectivity closes to unity. The possible reason is that the sorption of methanol could swell PVA membrane significantly. The swelling of methanol selective membranes by methanol has been reported in the literatures [42–44]. As the liquid solvent inside the membrane increases, the relaxation of polymer chain can occur and increases the size of free volume of the PVA membrane, therefore, the membrane lose its selectivity.

5. Conclusions

The application of pervaporation requires the understanding of coupling effects that may take place during the separation of multi-component mixtures. Two transesterification mixtures resulting from two model reactions have been taken as reference to evaluate this effect. Four commercial membranes containing different fractions of PVA have been studied.

Coupling effect is a complex phenomenon produced by the interaction among components and the interaction between components and membrane material. This phenomenon has been observed after comparing the membrane performance with pure solvents and two quaternary mixtures. The coupling effect can be explained with different approaches, which have been described in this work: a modification of the solubility of components in the polymer (described by Hansen solubility approach); and the change of the components activity within the membrane.

The modification of solubility due to the presence of other components can change the membrane performance. A pure component that is rejected by a membrane can be obtained in the permeate when it is present in a mixture as feed solution. Therefore, it suggests that the Hansen solubility parameters of mixture should be taken into account. The difference of activity coefficients considering the polymer and without the polymer were compared. It was found that the polymer material can enhance or reduce the activity, thereby, the driving force calculated within the polymer film is not identical to that calculated from the feed solution directly. The activity of each component within the membrane should also be analyzed in order to investigate the driving force within the membrane could be an important factor that motivates the mass transfer through the membrane.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.seppur.2017.12.041.

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