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Coupling effect during vapour permeation of organic mixtures through polymeric membranes

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ABSTRACT

A mass transport of organic compounds (benzene, hexane, cyclohexane and methanol) and their binary mixtures at wide activity range through dense semicrystalline low density polyethylene membranes is presented. Single and binary vapour permeation measurements were performed at 25°C and at 35°C by the differential flow permeation apparatus method connected with GC-MS device. Determined values of steady-state molar fluxes revealed the differences between single and binary permeation as well as the mutual coupling effect of second component in mixture on permeation flux of the first one.

Keywords: Vapour permeation; Binary mixtures; Coupling effect

1. Introduction

The detailed knowledge of the structure/permeability relations of polymers and information of their interactions with penetrants as well play an important role in industrial applications of polymer materials. In past decades, the membrane separation processes, as the low-cost energy-saving techniques, constituted a hopefully alternative to the classical technologies, especially in highly needed removal of volatile organic compounds (VOCs) from water or air [1–3]. Just the shortcomings and limitations of VOCs removal methods compels to searching of new polymer materials with better parameters (combining of rigid ''hard'' segments interspaced with flexible ''soft'' segments, imbedding of various-scale-fillers into polymer matrix etc) leading to the increasing of system performance (high selectivity, long lifetime, suitable mechanical properties) [1–3]. Therefore, many experimental studies of permeation, diffusion or sorption of gases and mainly vapors in polymers are performed to obtain information about transport parameters and decide possible polymer utilization. Hence, characterization of the mass transport of VOCs in and through polymer material is a complex process which beyond the external driving forces (temperature, pressure and concentration gradient) depends also on nature of polymer material and penetrating component. Therefore, for description of mass transport of gases and vapors through non-porous polymer membranes the solution-diffusion model [4] is frequently used. Based on this model, the mass transport process of one component through non-porous polymer membranes can be described as a sequence of consecutive processes of sorption of the components on the feed side of the membrane surface, activated diffusion through membrane and desorption of the components on the permeate side of the membrane. An association of diffusion with sorption (solubility) of permeation rate together in form

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$$P = D * S \tag{1}$$

where P is permeability coefficient, D is diffusion coefficient and S sorption coefficient.

For description of the multicomponent mass transport through polymer materials various forms of solutions are used, for instance extended 1st Fick law, linear irreversible thermodynamics or Maxwell-Stefan approach [1,5–8]. Hence, the isothermal-isobaric transport of binary mixture in form of molar fluxes J through finite membrane with gradient of chemical potential μ as driving force can be expressed as [7,9]

$$\begin{bmatrix} J_1 \\ J_2 \end{bmatrix} = -\begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \begin{bmatrix} \dfrac{\partial \mu_1}{\partial x} \\ \dfrac{\partial \mu_2}{\partial x} \end{bmatrix} \tag{2}$$

The off-diagonal phenomenological parameters L_{12} and L_{21} represent so called coupling effect caused by presence of the second component in mixture on transport of first component. Such mutual effects occurring in real systems could positively or negatively contribute to mass transport of components and therefore can play essential role in designing of appropriate industrial membrane process [1,3,9,10]. One of these membrane processes, pervaporation (PV), can be successfully used for separation of azeotropic mixtures [10,11], for instance PV of hydrocarbons with alcohols using low-density polyethylene membrane (LDPE) [12].

The aim of this work consists in illustration of the mutual influence of different-molecular-shape hydrocarbons and methanol on their transport properties in LDPE membrane

2. Experimental

2.1. Materials and chemicals

Low density polyethylene membrane BRALEN FB2-30 (LDPE) was supplied by Slovnaft, Slovakia. The thickness of antistatic membrane sample was 50 ± 1 μm. The degree of crystallinity was reported to be 45% and the density, determined by mercurial pycnometry, was $\rho = (919 \pm 2)\ \mathrm{kg\ m^{-3}}$ at 25°C [9]. Benzene, hexane, cyclohexane and methanol (p.a. grade, Sigma-Aldrich) were used without further purification. Hydrogen, carbon dioxide and helium (purity at least 99.99%) were purchased from Linde and SIAD and were used as received.

2.2. Vapour permeation measurements

For single and binary permeation experiments the differential flow permeameter was used [9,13,14]. The temperature-controlled measuring permeation cell (25°C) was partitioned by a flat circular membrane (13 $\mathrm{cm^2}$). Into the feed-side compartment was forced a constant H_2+vapour flux of 30 ml $\mathrm{min^{-1}}$ and on the permeate-side compartment was forced a pure H_2 flux. On both membrane sides was identical pressure (1.1 bar). Permeation of vapours through membrane led to changes of thermal conductivity of gaseous mixture in time on the permeate side, with respect to the value of pure H_2, were determined by a pair of thermistors built into a Wheatstone resistance bridge. From obtained transient experimental data was possible to evaluate values of diffusion coefficient D and from the steady-state data the values of permeability coefficient P. Measurements were carried out at different values of feed H_2 flux saturations, ranging from 10 to 100% with respect to each tested vapour pressure at given temperature (100% saturation means that vapour partial pressure in the H_2 stream is equal to the value of the vapour pressure at that given temperature). Before the first and between two subsequent measurements the membrane inside the cell was exposed to a H_2 flux for a period of 4 times the time of reaching the permeation steady-state (at least 2 h) in order to guarantee the complete removal of the previous species from the membrane. The accuracy of permeation measurements and determination of values of molar fluxes was found to be reproducible within 5–8%. Determination of binary mixtures by connected GC (Perkin Elmer-Arnel, USA) with mass spectrometer (Perkin Elmer, USA) was described previously [9].

3. Results and discussion

3.1. Permeability and diffusion coefficients

The permeability coefficients (in $[\mathrm{m^3(STP)\ m}]/[\mathrm{m^2\ s\ Pa}]$) of measured vapours [1,9,13] in appropriate concentration interval were calculated by:

$$P = \frac{k N_{\mathrm{ST}}\, \nu L}{p_{\mathrm{V}}} \frac{T_0\, p_{\mathrm{B}}}{A\, T p_0}, \tag{3}$$

where k is an apparatus constant (determined by calibration), N_{ST} is the voltage signal in steady-state, L is the membrane thickness, v the flow rate of the mixture, A is the membrane area, T is the temperature of experiment, T_0 is the standard temperature 273.15 K, p_0 is the standard pressure 101.325 kPa, p_{V} is the partial pressure of the vapours in the carrier gas (for gases $p_{\mathrm{V}} = p_{\mathrm{B}}$) and p_{B} is the barometric pressure. The effective (integral) diffusion coefficients were obtained from experimental data fitting ($n = 10$) by equation

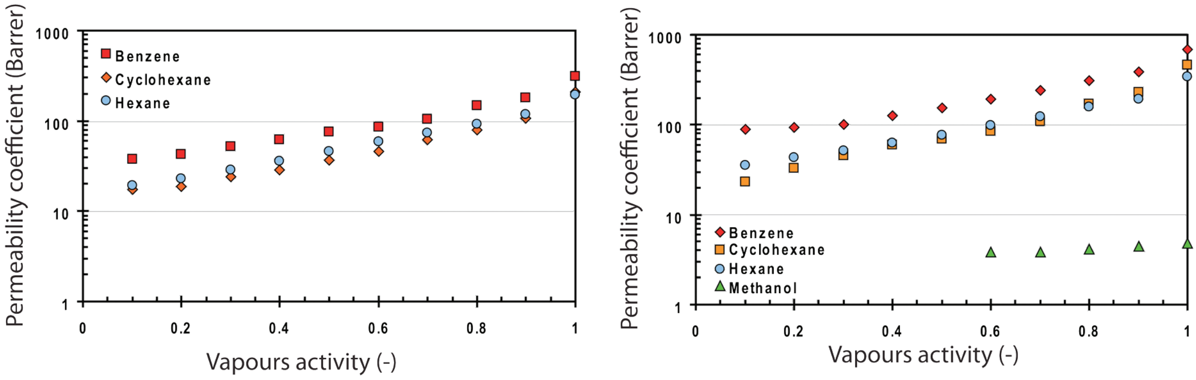

Fig. 1. Dependence of permeability coefficients on vapours activity at 25°C (left) and 35°C (right).

$$J(\tau) = \left(\frac{D c_1}{L}\right)\left[1 + 2\sum_{n=1}^{\infty}(-1)^n \exp\left(-\frac{D n^2 \pi^2 \tau}{L^2}\right)\right] \quad (4)$$

which was derived [15,16] from Fick's 2nd law under appropriate initial and boundary conditions and where the flux $J(\tau)$ through the membrane is measured as a function of time by a thermal-conductivity detector.

As expected on the basis of the sorption data [13], the permeation and diffusion of studied vapours in LDPE is a concentration-dependent process. While the permeability coefficients increased almost exponentially with increasing vapour activity (Fig. 1), the diffusion coefficients increased in a slightly sigmoidal fashion (Fig. 2). Both trends are in agreement with the literature [1,17] and the partial pressure of the vapours in the carrier gas corresponds to the appropriate vapours pressure at given temperature [13]. Thus, the effect of the carrier gas on the vapour permeation can be considered negligible (H_2:$D = 602.9\ 10^{-12}$ m^2 s^{-1}, $P = 9.47$ Barrer where 1 Barrer $= 7.5005\ 10^{-18}$ m^2 s^{-1} Pa^{-1}, S $= 1.177\ 10^{-7}$ cm$^3_{stp}$ cm^{-3} Pa^{-1}) [9] in comparison with the sorption and permeability of vapours. On Fig. 1 there are depicted the dependency permeability coefficients of vapours determined at two temperatures (298.15 K and 308.15 K). It is evident, that at higher temperature are determined permeability coefficient at same vapours activity higher nearly two times higher (in average benzene 2.2×, cyclohexane 1.9× and heptane 1.75×). Permeability coefficients of Methanol at 25°C were not evaluated because of too low vapours permeability. Despite the logarithmic scaling of graphs on Fig. 1 is clearly evident the dependence of permeability which is growing exponentially with increasing of vapours activity.

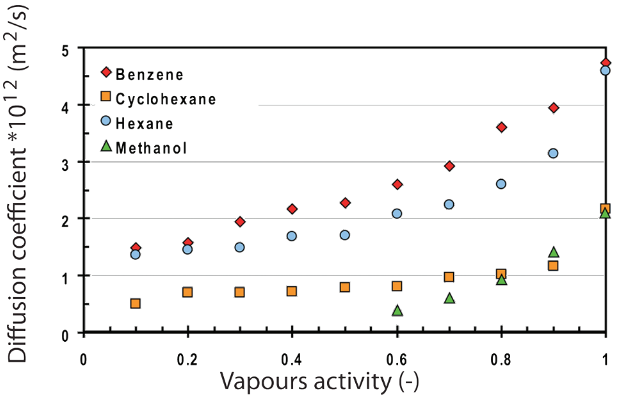

Fig. 2. Dependence of diffusion coefficients on vapours activity at 35°C.

The dependence of diffusion coefficient on vapours activity is shown on Fig. 2. In comparison with permeability, the increase of D values with vapours activity is not so strong while in case of permeation. Consequently, the determinative process of mass transport of vapours through LDPE membrane is a vapour sorption and corresponding interaction between polymer chains and penetrant molecules [9,13]. It is evident for comparison of hexane and cyclohexane; the permeability of both compounds is comparable, but the diffusion of hexane through LDPE is much faster. As follows from our previous works [13], the sorption of cyclohexane in LDPE exceeds even the sorption of benzene vapours.

3.2. Coupling effect

For the determination of the coupling effect from permeation experiments of binary mixtures the following arrangement was used: the concentration of the first compound was kept constant at a selected value while the second compound was added at different concentrations to form a predefined binary mixture [9]. The permeate side composition were determined by GC-MS and resulting molar fluxes of binary mixture components were afterwards confronted with the molar fluxes of the pure compounds at the same

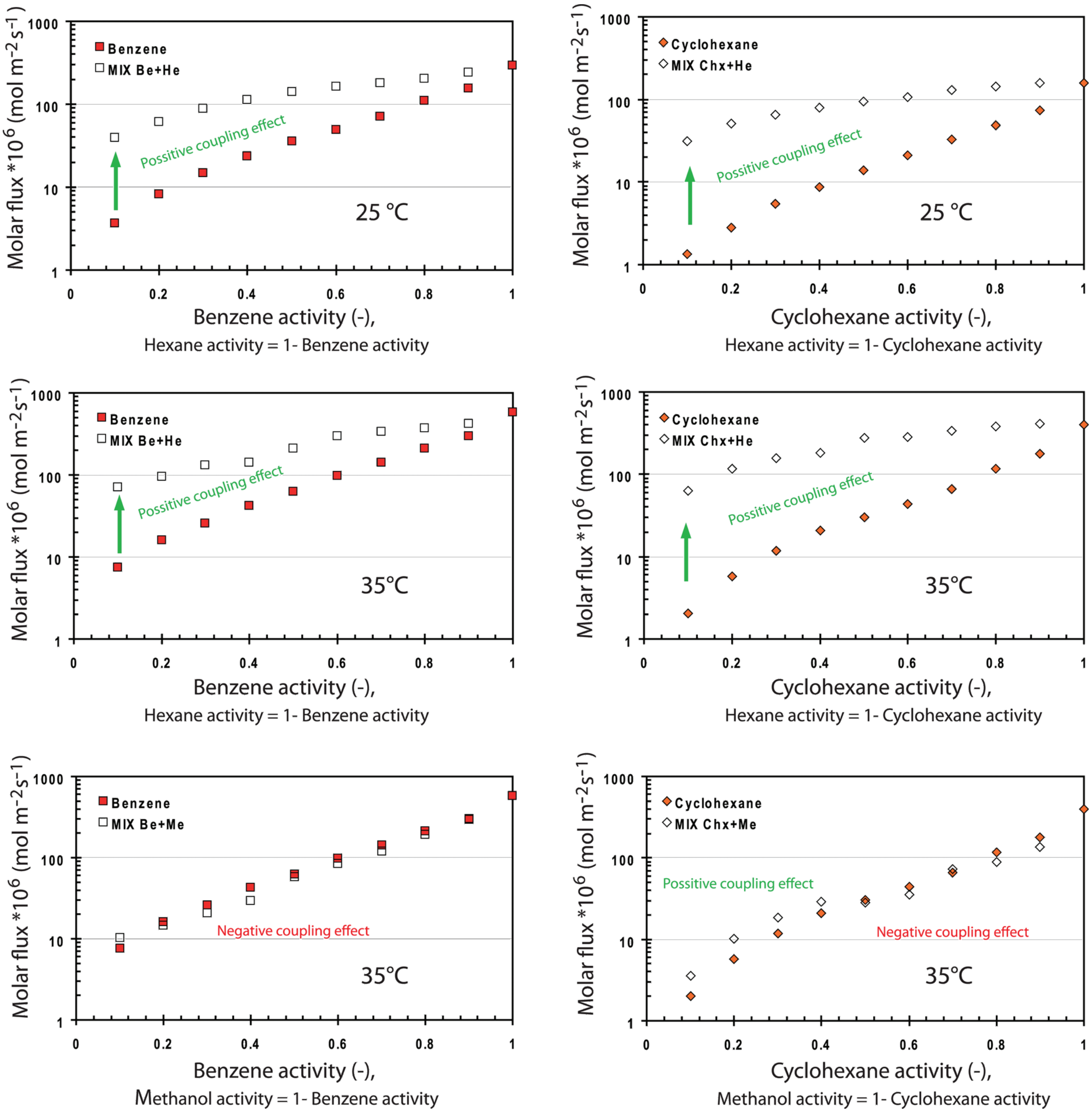

Fig. 3. Dependence of molar flux on vapours activity at 25°C and at 35°C.

activities. As it shown (Fig. 3), the presence of the second component in the mixture of benzene/hexane or cyclohexane/hexane influenced positively (positive coupling effect) the molar flux of the first compound the LDPE membrane. Such findings are in agreement with our previous work for toluene and heptane mixtures where the coupling effect determined from permeation and sorption experiments was found concentration-dependent. In permeation, the relative coupling effect, defined as a difference between determined molar flux of component in binary mixture minus calculated molar flux based on single compounds flux data and divided by molar flux of component in binary mixture [9], reaches nearly 50% and for sorption 16% [9]. Performing of binary mixtures at two temperatures revealed again the temperature effect on mass transport. In agreement with trend for permeation coefficients, also for higher temperature 35°C were determined higher molar fluxes.

For binary mixtures of benzene/methanol and cyclohexane/methanol such strong positive coupling effect was not observed, in addition the presence of low-sorbed less-penetrant-polymer-interacting methanol in mixtures caused sometimes reverse procedure (negative coupling) and the flux of hydrocarbons in binary mixture with methanol was lower in comparison with single vapour data at same activity.

4. Conclusions

The differential permeation technique was used for the investigation of the transport related phenomena in the binary mixture of organic vapours (benzene, hexane, cyclohexane and methanol) + LDPE system at two temperatures. Higher temperature caused higher permeability of studied vapours and higher molar fluxes through membrane as well. It was found that over the entire activity range the molar flux of the benzene/hexane and cyclohexane/hexane mixtures are significantly higher than the sum of the single components from corresponding measurements with pure vapours, indicating a marked positive coupling effect between hydrocarbons, while in mixtures of hydrocarbons with methanol the opposite process happen (negative coupling).

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