

Sorption of Binary Mixtures of Toluene + Lower Aliphatic Alcohols C₁ – C₆ in Low-Density Polyethylene

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ABSTRACT: Sorption gravimetric and volumetric techniques performed at 25°C and at atmospheric pressure were employed to study the preferential and total sorptions from binary liquid mixtures of toluene + lower aliphatic alcohols (C₁ – C₆) in a high-pressure low-density polyethylene membrane and the volume of the swollen membrane. Toluene was preferentially sorbed in all six systems. The total sorbed amount increased from pure alcohol to pure toluene. The experimental volume of the swollen membrane was compared

with that calculated under the assumption that interactions between the polymer and liquid mixture were negligible. The composition of the binary liquid mixture sorbed in the polymer as a function of the composition of the bulk solution surrounding the membrane is presented. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1781–1787, 2011

Key words: swelling; polyethylene (LDPE); membrane; phase diagrams; selectivity

INTRODUCTION

Mixtures of aromatic hydrocarbons (e.g., toluene) with aliphatic alcohols have wide use in the pharmaceutical industry¹ and are important in the fuel industry,^{2,3} where they are often used in fuels (alkanol is used as fuel additives and toluene represents original hydrocarbon fuel without additives²) and for verification of solution theories.⁴ Therefore, some physical properties of the binary toluene + aliphatic alcohols mixtures have been intensively studied. A thermodynamic study based on light scattering was published by Munk et al.⁵ and calorimetric data on excess calorimetric properties was reported by Mrazek,⁶ Hwa and Ziegler,⁷ and by Cobos et al.⁸ Vapor-liquid equilibria important for describing the distribution of compounds between vapour and liquid equilibrium phases at distillation and extraction separation processes can be found in^{4,9} (see comprehensive literature survey for limiting activity coefficients data presented by Vrbka et al.⁴). Distillation and extraction can be costly (extraction due to necessity of purification of extraction solvent); therefore, it

is important to consider cost-effective membrane separation processes. Nonequilibrium and equilibrium physical properties for transport of toluene + aliphatic alcohols have been studied. Mandal and Pangarkar¹ measured the dependence of the permeate composition on the feed content for pervaporation of methanol + benzene and methanol + toluene mixtures in the steady state through eight types of polymer membranes. Villaluenga et al.⁷ measured pervaporation characteristics for binary toluene + alcohol (methanol, ethanol or propan-1-ol) mixtures in linear low-density polyethylene (LDPE) membranes. Gagnard et al.³ reported the total permeation fluxes for toluene + methanol vapour mixtures in four polymer membranes. Data on the total mass uptake of pure toluene by LDPE were published by Makitra et al.¹⁰ and Corbin et al.,¹¹ the total mass uptake of pure aliphatic alcohols by LDPE was reported by Makitra et al.¹⁰ (ethanol, propan-1-ol, pentan-1-ol) and Cunha et al.¹²

The aim of this work was to extend the data available for binary toluene+(C₁ – C₆ alkan-1-ols) mixtures in contact with LDPE membranes. Measurements of preferential and total equilibrium sorption and equilibrium volumetric swelling were performed and are being reported for the first time.

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EXPERIMENTAL

Studied properties

The behavior of polymers in contact with various organics and the separation of organic mixtures

using polymeric membranes are challenging problems in many industrial fields.¹³ The separative performance of polymeric membranes is closely related to the membrane swelling and to preferential sorption phenomena.¹⁸

The swelling of polymeric materials is characterised by both weight and volume changes.²⁴ The respective swelling degrees are given by the following relations:

$$Q_m = \frac{m - m_0}{m_0} \quad (1)$$

$$Q_V = \frac{V - V_0}{V_0}, \quad (2)$$

where m_0 and V_0 and m and V are the masses and volumes of the dry and swollen polymer membrane, respectively.

However, most industrial applications and products include mixtures of more components; therefore, it is important to account for the special properties of multicomponent polymer–solvent mixtures. There is a basic difference between a binary system (i.e., a membrane and a pure liquid) and a ternary system (i.e., a binary liquid mixture and a membrane). In the latter case, the amount of the liquid inside the membrane (overall or total sorption) and especially the composition of the liquid mixture sorbed inside the membrane are important. Different affinities of the liquid mixture components towards the polymer²³ are responsible for the composition of the liquid mixture sorbed by a polymer being different than the composition of the bulk liquid mixture surrounding the polymer. The extent of this difference is expressed by the preferential sorption. In all of the LDPE + toluene + alcohol systems studied herein, the sorbed liquid was enriched on toluene (i.e., toluene is preferentially sorbed). The relationship for the toluene preferential sorption is

$$\Omega_T = n^s (x_T^s - x_T^b), \quad (3)$$

which describes the difference in the number of moles of toluene (subscript T) contained in n^s moles of the liquid mixture sorbed in the polymer (superscript s) and those contained in the same total number of moles of the bulk solution (superscript b), which are all related to the unit of mass of the dry polymer. Based on experimental data for the change in the bulk solution composition, the preferential sorption can be described as:

$$\Omega_T = n_0 \cdot (x_{T,0}^b - x_T^b), \quad (4)$$

where n_0 is the number of moles of the initial binary solution per 1 g of dry polymer, and $x_{T,0}^b$ and x_T^b

are the molar fractions of toluene in the bulk initial and equilibrium solutions, respectively. The total amount of binary liquid sorbed in 1 g of a dry polymer (n^s) can be expressed from the weight uptake

$$n^s = \frac{Q_m}{\bar{M}^s} = \frac{Q_m}{x_T^s M_T + (1 - x_T^s) M_A}, \quad (5)$$

where \bar{M}^s is the average molar mass of the binary sorbed liquid, M_T and M_A are the molar masses of the pure components ($T = \text{toluene}$ and $A = 1$ to 6 for alcohols, methanol to hexan-1-ol).

Equations (3) and (5) allow for the expression of the directly immeasurable composition of the liquid sorbed in the polymer phase by using experimental data on preferential and total sorptions [Eqs. (1) and (4)]

$$x_T^s = \frac{Q_m x_T^b + \Omega_T M_A}{\Omega_T (M_A - M_T) + Q_m} \quad (6)$$

Materials and sample preparation

The high-pressure LDPE film used in this study was BRALEN FB 2–30, which was provided by Slovnaft a.s., Bratislava, Slovak Republic (material characteristics given by manufacturer: melt mass-flow rate = 2 g/10 min, tensile properties (ISO 527) = 22/17 MPa, Vicat softening temperature = 96°C, opacity = 8%). The thickness of the dry foil, 0.046 mm, was measured by an Inductive Dial Indicator Mahr (Germany) and its density, 0.940 g cm⁻³, was determined by weighing a sample of known area and thickness. Samples were cut from the large polymer sheets, thoroughly rinsed with distilled water, dried in a laboratory oven at 60°C for 20 h, and stored in a vacuum desiccator at 25°C until further use. A fresh membrane sample was used for each measurement.

All solvents (Table I) were p.a. purity grade and were provided by Sigma-Aldrich. Their densities were determined using a DMA 5000 Anton Paar densimeter and are in good agreement with tabulated values²⁸ (see Table I).

Sorption experiments

All experiments were carried out at 25°C and at atmospheric pressure. The total amount of the sorbed liquid has been determined by a gravimetric method.^{29,30} A preweighed circular disc-shaped membrane sample of the dry polymer (diameter of 6 cm) was immersed into an excessive amount ($m_{\text{solution}}/m_{\text{polymer}} = 300$) of the respective solvent mixture of an exactly known composition in a tightly sealed flask and allowed to reach sorption equilibrium. The

TABLE I
Properties of Liquid Solvents at 25°C

Solvent	M (g mol ⁻¹)	ρ (g cm ⁻³)	
		This work	TRC Tables ²⁸
Toluene	92.14	0.86241	0.8622
Methanol	32.04	0.78707	0.78664
Ethanol	46.07	0.78630	0.78509
Propan-1-ol	60.09	0.79987	0.79975
Butan-1-ol	74.12	0.80604	0.806
Pentan-1-ol	88.15	0.81130	0.8115
Hexan-1-ol	102.17	0.81550	0.8162

wet membrane sample was then transferred into a weighing bottle lined with filter paper and arranged in such a position that only its edges touched the paper. The full bottle was weighed after about 1 h, when the paper had drained off the excess liquid from the membrane and the equilibrium in the bottle was established. The foil was then quickly taken out and the bottle with the wet paper was weighed again. The difference represented the weight of the swollen foil (m). This procedure was found to be reproducible to ± 2 mg. The results are expressed as the mass swelling degree Q_m [Eq. (1)].

To determine the preferential sorption, the change in toluene concentration in the bulk solution brought about by its contact with polymer was measured. Exactly weighed amounts of the dry polymeric foil cut in small pieces and of the binary liquid solution with a known composition ($m_{\text{solution}}/m_{\text{polymer}} \approx 3$) in a tightly sealed bottle were kept at constant temperature for 24 h and stirred often. The difference in toluene content in the initial and equilibrium solutions, $x_{T,0}^b - x_T^b$, was then determined using the Rayleigh-Haber-Lowe differential interferometer (Carl Zeiss, Germany) with a 0.5-cm double cell (maximum difference in the molar fractions ± 0.02).¹⁸ The preferential sorption was calculated from Eq. (4).

Volumetric measurements

The volume of the swollen membrane, V^{exp} , was determined from the dimensional changes of the square membrane samples (1 × 1 cm) cut off in parallel with the edges of the membrane sheet supplied by the manufacturer. Two dimensions in the plane of the membrane sheet were monitored directly in liquid by the optical method, which has been described in our previous papers.³¹ The third dimension, thickness, was measured immediately after taking the membrane out of the liquid by an Inductive Dial Indicator Mahr. The experimental errors in the percentage relative expansion were determined to be ± 1 and ± 2 for the optical and thickness measurements, respectively.

RESULTS AND DISCUSSION

Total sorption

Figure 1 shows the equilibrium swelling degrees Q_m for all six systems under study, which were obtained as the relative weight gain and plotted as a function of the bulk solution composition. The Q_m values are expressed as the molar fraction of toluene.

The greatest swelling effect was observed in pure toluene ($Q_m = 0.213$). This value is in good agreement with the value of 0.22, which was calculated¹⁰ from Richards' data (vol %),³⁵ but is greater than $Q_m = 0.17$, which was reported¹¹ as an approximate value for 0.075-cm-thick LDPE. The swelling degrees of polyethylene in pure alcohols were considerably smaller. Their values increased with the number of carbon atoms from methanol to hexan-1-ol in accordance with the lipophilicity trend of the alcohols (expressed by the octan-1-ol/water partition coefficients³⁶) as shown in Figure 2. The swelling degree of LDPE in methanol, $Q_m = 0.011$ obtained in this work at 25°C can be compared only with the values of 0.018 at 30°C and 0.019 at 45°C by gravimetric method¹² for LDPE foils 20 and 35 μm thick (the results were the same for both samples). The only data found in literature for polyethylene swelling in other alcohols were reported by Makitra et al.¹⁰ for ethanol, propan-1-ol, and pentan-1-ol, and were calculated from Richards' data.³⁵ However, these values are one-order smaller than ours.

With increasing contents of toluene in the bulk solution, the total liquid uptake increased. From systems with methanol to those with hexan-1-ol, we observed only small differences in the swelling

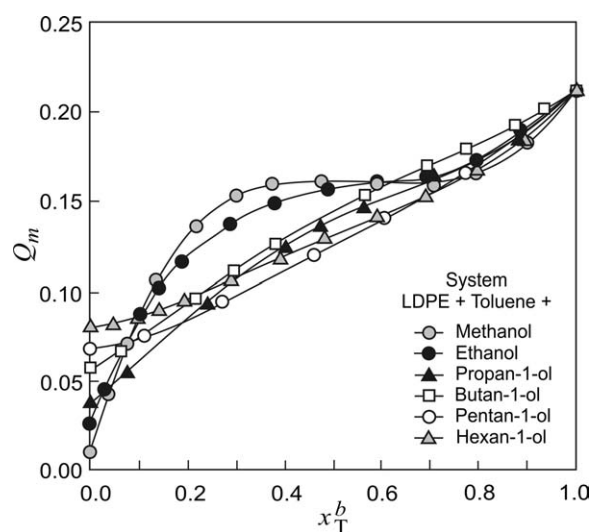


Figure 1 Mass equilibrium swelling degree Q_m of LDPE as a function of the bulk solution composition in the toluene + alkan-1-ol systems (molar fraction of toluene) at 25°C; manually drawn curves connect the experimental points to outline the trend in the data.

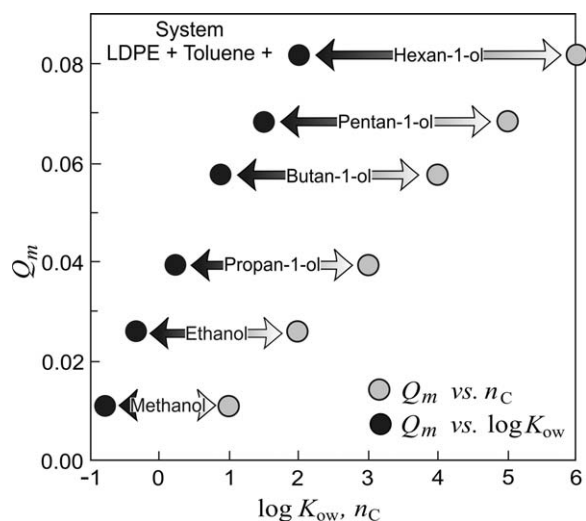


Figure 2 Mass equilibrium swelling degree Q_m of LDPE in pure C_1 to C_6 alcohols correlated with the length of alcohol carbon chain (n_c) and with octan-1-ol/water partition coefficients³⁶ at 25°C.

degree values at toluene concentrations exceeding 60 mol %, suggesting that toluene has a prevailing role in polyethylene swelling in this concentration range. The same conclusion was drawn from the correlation of the swelling degree with the Hildebrand solubility parameters^{37–39} (Fig. 3). Between 10 and 50 mol % of toluene, the effect of toluene was most pronounced in the LDPE + toluene + methanol and LDPE + toluene + ethanol systems compared with those with other alcohols. These results were likely caused by the sorption of excess toluene in systems with short chains in this concentration range. The existence of the excess toluene follows from the dependence of preferential sorption (see Fig. 6).

Volume changes

In actual applications, the dimensional response of the membrane is important to assess its solvent resistivity. The solvent ingresses the membrane, occupies the free volume spaces within the matrix, and the volume dilations of the matrix material occurs due to interactions of the solvent molecules with the polymer chain segments.^{27,40} The assumption of additivity leads to the following expression:

$$V^{\text{add}} = \frac{1}{\rho} + n^s (x_T^s \cdot V_{mT} + x_A^s \cdot V_{mA} + V^E), \quad (7)$$

where V^{add} is the volume of the swollen membrane and is related to 1 g of the dry polymer ($\text{cm}^3 \text{g}^{-1}$); ρ the density of dry polymer (g cm^{-3}); n^s the equilibrium mole number of liquid sorbed in 1 g of dry membrane (mol g^{-1}) and is calculated from the weight uptake [Eq. (5)]; V_{mT} , V_{mA} are molar volumes of pure

liquid penetrants: toluene (T) and alcohol $A = 1-6$ (methanol to hexan-1-ol) ($\text{cm}^3 \text{mol}^{-1}$); and V^E is the excess molar volume of the binary solvent.^{43–47}

The measurements of the dimensional changes revealed that there were differences between the real volume of the swollen membrane, V^{exp} , and V^{add} , which was calculated from Eq. (7). The comparison of the experimental and calculated volume values is presented in Figure 4. The highest values of the volume difference $V^{\text{add}} - V^{\text{exp}}$ were observed in the LDPE + toluene + methanol system. The difference diminished for longer alcohols, indicating that methanol caused the strongest polymer – liquid medium interactions due to its most pronounced hydrophilic character (methanol is the only alcohol where the hydroxyl group is bulkier and heavier than the alkyl chain). This interpretation based on the polymer – liquid interactions is in accordance with the trends in limiting activity coefficients of alkan-1-ols in alkanes.⁴⁸ The values of limiting activity coefficients decrease from methanol to hexan-1-ol for the same alkane, reflecting that the interactions between alcohol and hydrocarbon chain also diminish in this direction.

Figure 5 shows the concentration dependence of the swelling degree Q_V as the relative volume increased [Eq. (2)] based on dimensional measurements.

Preferential sorption

The experimental data on the concentration changes of the bulk solution, which were caused by the sorption of binary liquid mixtures in LDPE, were plotted as composite isotherms, i.e., the preferential sorption, calculated from Eq. (4) against the equilibrium bulk solution composition. The composite isotherms

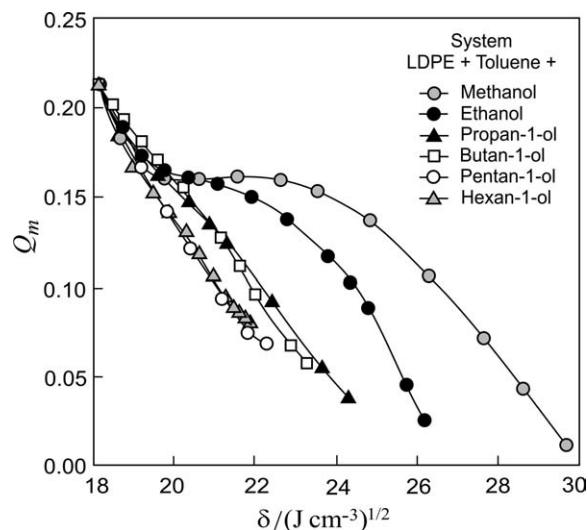


Figure 3 Mass equilibrium swelling degree Q_m of LDPE in mixtures toluene + (C_1 – C_6) alcohols correlated with Hildebrand solubility parameters³⁷ at 25°C.

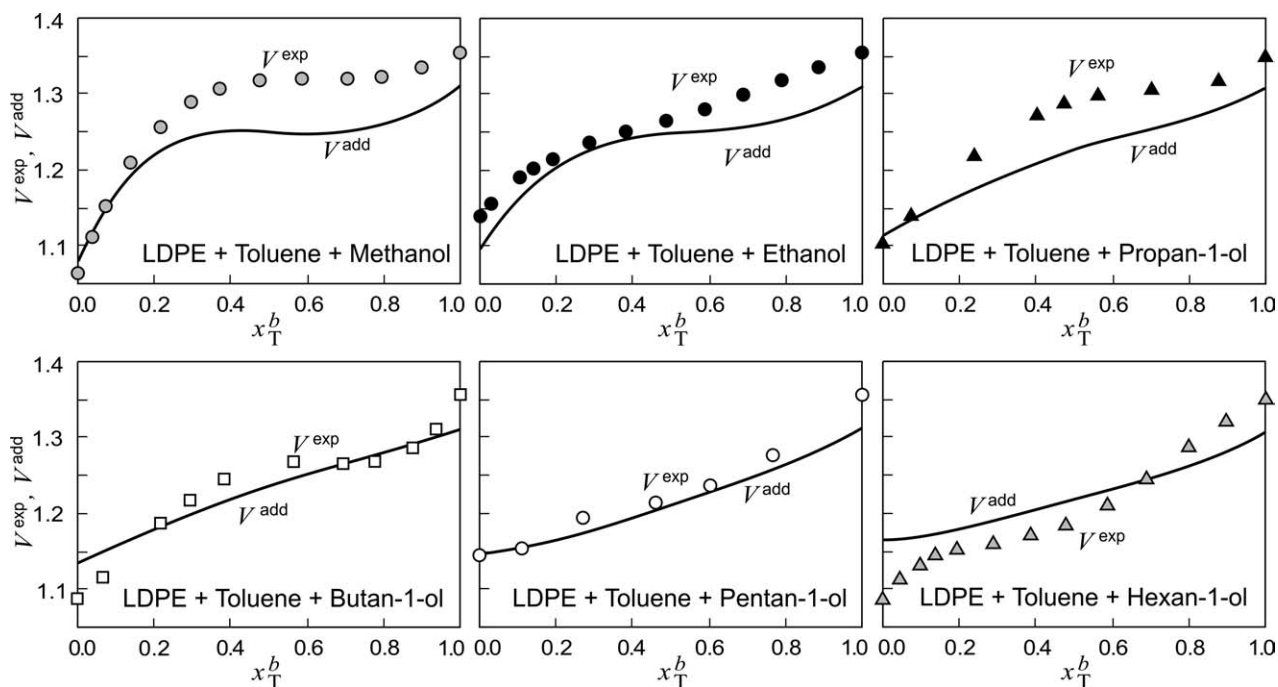


Figure 4 The comparison of the experimental volume of the swollen membrane (V^{exp} -points) and its volume calculated from Eq. (7), assuming additivity (V^{add} -full line) at 25°C.

(Fig. 6) were of the common n-shape for all six studied systems. In accordance with the increasing difference in the lipophilities of toluene and alcohol when going from hexan-1-ol to methanol, the maximum on the composite isotherm was highest for the LDPE + toluene + methanol system. Because the influence of the polar OH-group diminishes with increasing C-chain length in the alcohol molecule, the maximum value of the preferential sorption decreased. In addition, the position of the maximum shifted to higher toluene contents (from $x_T^b \cong 0.3$ for

LDPE + toluene + methanol to $x_T^b \cong 0.5$ for LDPE + toluene + hexan-1-ol). At higher toluene concentrations (above $x_T^b \cong 0.6$), there were only small differences in the preferential sorption values for individual systems. To our knowledge, no previous studies have reported on the preferential sorption in LDPE + toluene + alcohol ($C_1 - C_6$) systems.

To illustrate the composition changes of the binary liquid mixture on its entering into the polymer, a phase diagram showing the relationship between the molar fractions of toluene in the sorbed liquid

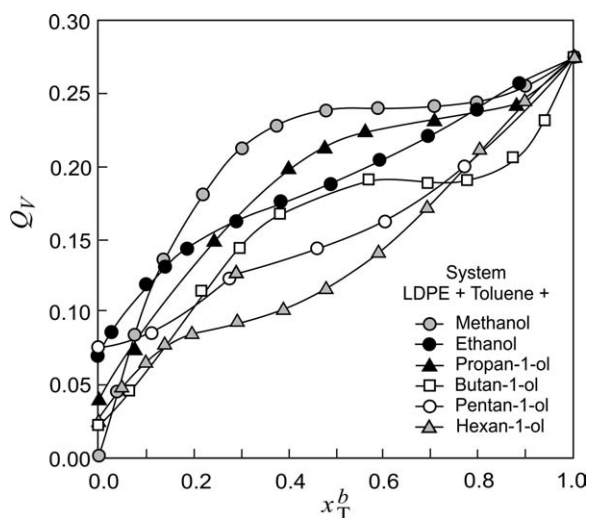


Figure 5 The volume equilibrium swelling degree Q_V of LDPE as a function of bulk molar fraction of toluene in the toluene + alkan-1-ol systems at 25°C.

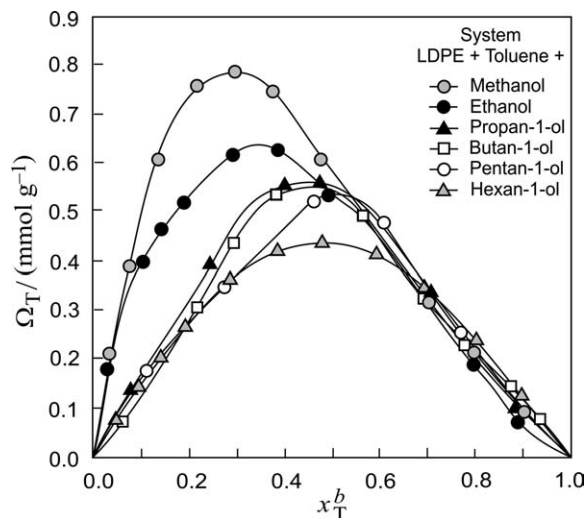


Figure 6 The preferential sorption Ω_T of toluene in LDPE as a function of bulk equilibrium molar fraction of toluene in the toluene + alkan-1-ol systems at 25°C.

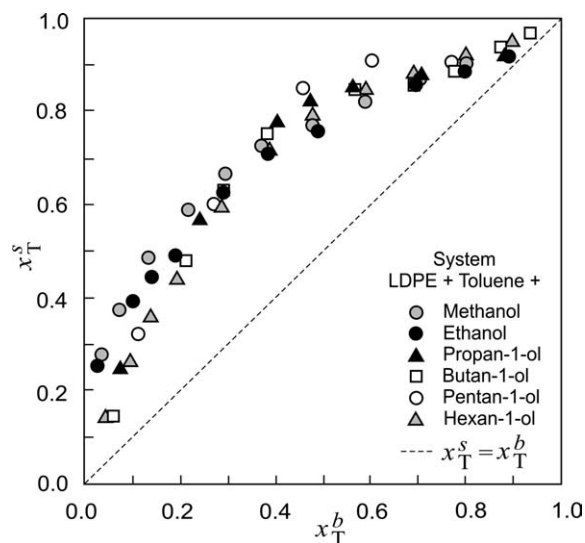


Figure 7 The sorption equilibrium in the systems LDPE + toluene + alcohol at 25°C. The relationship between the composition of the liquid mixture inside the swollen LDPE membrane and the composition of the bulk solution surrounding the membrane.

mixture, x_T^s , and those in the bulk solution, x_T^b , is shown in Figure 7. Notably, the points representing all six systems lie within a narrow range; a more narrow range indicates a greater concentration of toluene in the bulk solution. The x_T^s vs. x_T^b curve for the methanol + toluene + LDPE system can be compared with the dependence of permeate composition vs. feed composition derived from pervaporation data.¹ The shape of both dependencies is similar, thereby confirming that equilibrium sorption data can be used as a criterion of selectivity for membrane separation processes despite that membrane separation processes are more complex (consisting of steady-state dynamic processes, diffusion and desorption).

CONCLUSIONS

Herein, we presented the results of weight uptake measurements for the LDPE foil (thickness of 46 μm) on its immersion in six binary liquid mixtures of toluene with lower aliphatic alcohols ($C_1 - C_6$) over the whole concentration range at 25°C and atmospheric pressure. Low values of the swelling degree were observed in pure alcohols (from $Q_m = 0.011$ in methanol to 0.082 in hexan-1-ol, increasing with decreasing polarity of the alcohol). With increasing concentration of toluene in the liquid mixture, the total liquid uptake increased up to $Q_m = 0.213$ in pure toluene. Preferential sorption measurements revealed that the toluene affinity to LDPE is higher than the affinity of any alcohols. In addition, the composition isotherms were n-shaped. The maximum value of the preferential sorption decreased in magnitude

from the system with methanol ($\Omega_T = 0.78 \text{ mmol g}^{-1}$) to that with hexan-1-ol ($\Omega_T = 0.44 \text{ mmol g}^{-1}$) and the position of this maximum shifted towards increasing concentrations of toluene in the bulk solution from $x_T^b = 0.3$ to $x_T^b = 0.48$. At toluene concentrations of $x_T^b > 0.6$, there were only small differences in the values of the toluene preferential sorption in the studied systems, indicating the prevailing influence of toluene on sorption phenomena in this concentration range.

The dimensional response data revealed that the changes in membrane volume are caused not only by the entrance of a certain amount of liquid into the membrane but also by interactions between the polymer and solvent. These interactions are the strongest in the system with methanol and very weak in the system LDPE + toluene + pentan-1-ol.

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