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Šercl, Jonatan, Shimizu, Seishi orcid.org/0000-0002-7853-1683 and Vopička, Ondřej (2025) Isomer-specific sorption of C8H10 aromatics in Matrimid®. Colloids and surfaces a-Physicochemical and engineering aspects. 137569. ISSN 0927-7757

https://doi.org/10.1016/j.colsurfa.2025.137569

Isomer-specific sorption of C_8H_{10} aromatics in Matrimid®

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ABSTRACT

Sorption of four C_8H_{10} isomers (ethylbenzene, *o*-, *m*-, *p*-xylene) in Matrimid® films has been studied to screen its potential applicability as a sorbent. Uptakes for single-component liquids in Matrimid® followed the order *o*-xylene > *p*-xylene > *m*-xylene ≈ ethylbenzene. A new technique was developed to measure liquid uptakes in polymer films. Selectivity for *o*-xylene over ethylbenzene was found for the sorption of the equimolar quaternary liquid mixture. Binary mixtures of *o*-xylene and ethylbenzene showed a separation factor of 1.19 ± 0.05. Vapor sorption isotherms for the pure sorptives followed the recently derived ABC model based on the statistical thermodynamic fluctuation theory. Vapor sorption kinetics corresponded to the non-Fickian diffusion and was slower than that for the liquid sorption. All three contributions (mono-, di-, tri-sorbate interactions with sorbent, A^{-1}, B, and C) were necessary to fit the vapor sorption data. Only the mono-sorbate – sorbent interaction parameter (A^{-1}) was needed to fit sorption data for the liquid mixtures and pure liquids. Overall, Matrimid® contains moieties with specificity to constitutional isomers, and undergoes physical relaxation upon its exposure to C_8H_{10} liquids. Focused research can lead to further optimized polyimides for the separations of hard-to-separate mixtures, here close-boiling aromatics.

Introduction

The separation of the mixtures of BTEX (benzene, toluene, ethylbenzene, xylenes) compounds using rectification is complicated by the similarity of boiling points [1, 2]. This led to the development of specialized techniques [3-8]. For instance, chromatographic and membrane-based methods rely on materials exhibiting sorption or diffusion selectivity to the compounds of interest, chiefly *p*-xylene, while optimization of materials (adsorbents, membrane materials) and conditions (temperature, pressure) is crucial to reach the application level. We report a survey on the sorption and diffusion characteristics of Matrimid® films for four C_8H_{10} isomers (ethylbenzene, *o*-, *m*-, *p*-xylene) at mild conditions (35 °C), and demonstrate the usability of the ABC modeling approach [9]. Although real feedstocks can contain also other compounds (benzene, toluene, C_9 aromatics, etc. [10]), we see this choice as a meaningful simplification. Given its thermal (glass transition at 313 °C [11, 12]), chemical, and mechanical stability, solvent-processability, plasticization resistance, and ability to form dense films, Matrimid® is a promising glassy polymer that could support advances in both chromatographic and membrane-based separation techniques.

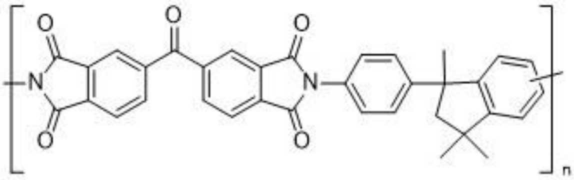

Fig. 1. Chemical structure of repeat unit of Matrimid® 5218 [13], that is BTDA-DAPI (poly(3,3’-4,4’-benzophenone tetracarboxylic‑dianhydride diaminophenylindane).

SORPTION

Sorption kinetics for single sorptive

Assuming Fickian diffusion, the sorption kinetics for a film subjected to a stepwise change of concentration (with respect to time τ) can be described by the following expressions differing in the convergence behavior [14, 15]:

$$\frac{Q(\tau)}{Q_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \mathrm{e}^{\frac{-D(2n+1)^2\pi^2\tau}{l^2}} = 4\sqrt{\frac{D\tau}{l^2}}\left\{\frac{1}{\sqrt{\pi}} + 2\sum_{n=1}^{\infty}(-1)^n \operatorname{ierfc}\frac{nl}{2\sqrt{D\tau}}\right\} \tag{1}$$

in which Q is total sorbate quantity (mass) in the film per its mass, l the film thickness, n index, and D diffusivity. The relative uptake according to Eq. (1) is proportional to $\tau^{0.5}$ when τ is small [see the right-hand-side of Eq. (1)]. Polymer glasses frequently show anomalously fast diffusion, for which the relative total sorbate quantity is proportional to τ^N with N ranging from 0.5 to 1. This phenomenon onsets after a certain period of Fickian behavior described by Eq. (1), and involves the sorbate-induced relaxation of the glass . The limiting case is the case II diffusion, for which $N = 1$ and sharp boundary separating the swollen and dry polymer moves in the film at a constant velocity. While the principles governing the non-Fickian diffusion are rather clear, its exact modeling is rather complex [12, 16-20]. In this work, the sorption kinetics is used to detect the apparent sorption equilibrium, for which the system properties are analyzed in detail.

Sorption uptakes at apparent equilibrium

At apparent equilibrium, sorption uptakes of species in a sorbent can be expressed using the recently developed ABC model [9]. This model, grounded in the statistical thermodynamic fluctuation theory [21], generalizes the commonly used models (such as GAB, BET, Langmuirs's case I, *etc.*) by eliminating their overly idealized assumptions (*e.g.* unrestricted layer-by-layer adsorption), and effectively captures even anomalous isotherms [22]. This physical model is a viable computationally effective alternative to the up-to-date molecular dynamics simulations [23-26], for which the slow relaxation, common for glassy materials, appears an issue. Via an interfacial generalization of the Kirkwood-Buff theory of solutions [27], the theory enables the modeling of sorption for both vapors and liquids [21, 28] in a parallel manner. According to IUPAC [29, 30], sorption uptake can be expressed as the specific surface excess m_2^σ/m, while compound 2 in the sorbed state is the sorbate, the sorptive is the same component in the fluid phase, m is mass of the sorbent. The assessment of the specific surface area at the conditions of the experiment may be questionable for a swelling polymer [29], the specific surface excess is measurable (see below) and thus practical in this work. Interestingly, dense Matrimid® films contain micropores of sizes [31, 32] comparable with the molecular diameters of the studied compounds [8]. Consequently, sorbate molecules present in the pores do not resemble bulk liquid or vapor; its structure is affected by the presence of the pores. The fluctuation theory is capable of characterizing such pore-induced change in the sorbate structure [21, 22]. Specific surface excess can be expressed for the single sorptive (2, vapor) using the ABC isotherm:

$$\frac{m_2^\sigma}{m} = \frac{a_2}{A_2 - B_2 a_2 - \frac{C_2}{2} a_2^2} \tag{2}$$

Parameters A^{-1}, B, and C represent the mono-, di-, and tri-sorbate interactions at the sorbent, a_2 is activity or the pressure relative to at the saturated vapor pressure with neglect of the Poynting correction. We will demonstrate that the parameter A in Eq. (2) can be determined, via swelling measurements, also for single sorptives (2, liquid) that agree quantitatively with those determined from liquid mixtures when B and C are negligible, just as in the case of liquid mixtures (as will be demonstrated below).

The Kirkwood-Buff χ parameter, i.e., the generalization of the Flory χ parameter beyond the lattice model, can be calculated [22, 32, 33] via

$$\chi = 1 - \frac{\partial}{\partial a_2} \frac{a_2 m}{m_2^\sigma} = (B_2 - 1) + C_2 a_2 \tag{3}$$

For a binary liquid mixture of sorptive and solvent, the specific relative surface excess of sorbate (2) (further *o*-xylene unless single sorbate is studied – see Table 1, Fig. 2, and Fig. 3) with respect to solvent (1) (ethylbenzene unless stated otherwise) has the form [28]

$$\frac{m_2^{\sigma(1)}}{m} = \frac{m_2^{\sigma}}{m} - \frac{m_1^{\sigma}}{m}\frac{w_2^{\text{liq}}}{w_1^{\text{liq}}} = \frac{1}{m}\left(m_2^{\sigma} - m_1^{\sigma}\frac{w_2^{\text{liq}}}{w_1^{\text{liq}}}\right) = \frac{a_2}{A_2^{\text{rel}} - B_2^{\text{rel}}a_2 - \frac{C_2^{\text{rel}}}{2}a_2^2} \tag{4}$$

where w stands for mass fraction. By noting that a_2 here refers to the activity of sorptive in the sorptive-solvent mixture, how the ABC parameters should be interpreted for non-ideal solutions has been clarified (see SI: Section E of form [28]). For the studied compounds, molar and mass fractions are equal due to the equality of molar masses, $w_2^{\text{liq.}} = x_2^{\text{liq.}}$. Moreover, the liquid solutions of the constitutional isomers *o*-xylene and ethylbenzene are close to thermodynamic ideality, thus $a_2 = w_2^{\text{liq.}}$ in this work. Specific reduced surface excess $m_2^{\sigma(m)}/m$ is calculated [29] as

$$\frac{m_2^{\sigma(m)}}{m} = \frac{m_2^{\sigma(1)}}{m}w_1^{\text{liq}} \tag{5}$$

Separation factor [29] comparing the compositions of the sorbate and the liquid has the form

$$S = \frac{m_2^{\sigma}/m_1^{\sigma}}{w_2^{\text{liq}}/w_1^{\text{liq}}} \tag{6}$$

The sorption of a binary liquid mixture (compounds 1 and 2) in a solid insoluble polymer (3) can be viewed as solid phase extraction. Note that the chemical potentials of species 1 and 2 are the same between the interface and the bulk in the Gibbs isotherm [34]. Consequently, the bulk solution dictates the mixing thermodynamics of species 1 and 2, for which the deviation from ideality for isomer mixtures can be neglected [35], and the activity coefficients in the bulk can be set to 1. However, the composition of the mixture changes under preferential sorption onto the insoluble polymer. Following the common practice of considering sorbed mixture as a "phase", we can estimate the activity coefficient of compound 2, γ_2^{σ}, at the insoluble polymer, via

$$\gamma_2^{\sigma} = \frac{w_2^{\text{liq}}}{w_2^{\sigma}} = \frac{1}{K_2} = \frac{w_2^{\text{liq.}}}{m_2^{\sigma}}(1 + m_1^{\sigma} + m_2^{\sigma}) \tag{7}$$

Expression for compound 1 is analogous, K_2 is Nernst distribution coefficient.

The Kirkwood-Buff χ parameter is a measure of self-interaction compared to the mutual that can be applied for the two cases: interface (σ) and bulk liquid (liq). Their dependence on the specific relative surface excess of sorbate (2) and specific surface excesses of sorbate and solvent (2, 1) can be found in the literature [28], thus

$$\frac{\partial}{\partial a_2}\frac{a_2}{\frac{m_2^{\sigma(1)}}{m}} = -\frac{S^2(\chi^\sigma + 1) - (\chi^{\mathrm{liq}} + 1)}{\frac{m_1^\sigma}{m}(S - 1)} \tag{8}$$

MATERIALS AND METHODS

Materials

Dense films from Matrimid® 9725 (a micropulverized form of Matrimid® 5218, Huntsman) were prepared by casting its 1.5 wt% solution in dichloromethane (DCM, 99.92 wt%, Lachner) onto a glass Petri dish and covered. Evaporation took 3 days, the film was then submerged into the excess of liquid methanol to remove the entrapped DCM (1 day, ambient temperature) and set the physical state of the material; see [12] for details. The sample was then dried in a vacuum (35 °C, Binder VDL, Pfeiffer HiScroll 12) for one day. Methanol (99.93 wt.%, Lachner), ethylbenzene (99.9 wt.%, Acros), *o*-xylene (99.3 wt.%, Acros), *m*-xylene (99.8 wt.%, Acros), *p*-xylene (99.9 wt.%, Acros), liquid nitrogen (Siad), helium (4.8, Siad), nitrogen (4.0, Siad), hydrogen (4.5, Siad) and air (technical, Siad) were used as obtained. Chemical analyses were done using a gas chromatograph (GC) (Thermo Scientific Trace 1300) equipped with a capillary column (TG-WaxMS), and a FID detector.

Vapor sorption microgravimetry

Vapor sorption was studied using a previously reported [12] microgravimetry device. The sample was maintained at a constant temperature (35.0 ± 0.1) °C and exposed to vacuum (< 0.01 Pa, Leybold D4B) or to the vapor of the studied compound (without air or other inert gases) at a chosen constant pressure (Leybold CTR 90). Average uncertainty of sorption uptake was 10 mg/g.

Liquid sorption

Single-component liquid sorption was measured using the previously reported method [36]. The dried film was immersed in excess of the liquid and incubated in a glass vial placed in a metal block maintained at 35.0 °C for two days. After incubation, the sample was taken from the liquid, the free liquid was removed with a blotting paper. The sample was then placed onto a metal mesh and weighed repeatedly in ambient air (Ohaus DV215CD) over time for approx. 10 min. The mass of the equilibrated sample (at the time of the sample removal from the liquid) was extrapolated. Average sorption uptake had an uncertainty of 40 mg/g. To prepare for subsequent measurements with a different liquid, the sample was submerged in the excess of liquid methanol for one day, and vacuum-dried at 35.0 °C for one day.

The sorption of liquid mixtures of *o*-xylene (subscript 2, sorptive) and ethylbenzene (subscript 1, solvent) was measured in two steps. The first step was analogous to the above measurement with single-component liquids. The sample was immersed in the liquid mixture of *o*-xylene and ethylbenzene for at least two days (the typical time of incubation was 4 days). After weighing (see above), the sample was again immersed into the same liquid mixture (*o*-xylene and ethylbenzene) and incubated for one day. A sample of the liquid was then taken into GC. The swollen polymer was then removed, cleared from free liquid, and immersed into the excess of liquid methanol. After incubation for one day, the methanolic solution was analyzed using GC. This method enabled us to derive specific surface excess, see Eq. (2), for the case of liquid mixture sorption, which appears uncommon [29]. Typical dosages were 0.01-0.02 g of Matrimid® film, 7 g of the C_8H_{10} liquid, 1-2 g of liquid methanol. Two series with two independent samples were conducted to prove the repeatability of the results and sufficiency of the incubation time, see Results and discussion below, details are provided in the Supplementary Dataset (SD).

Wide-angle X-ray scattering

Wide-angle X-ray scattering (WAXS) patterns were measured for a film (120 ± 5) μm thick using a PANalytical X'Pert PRO (Cu-Kα). The measuring sequence was conducted with one sample as follows. *i*) Sample was submerged into excess of liquid methanol (1 day, ambient temperature), then vacuum-dried (1 day), WAXS scan was performed. *ii*) The sample was submerged in excess of liquid ethylbenzene (1 day, ambient temperature), then fixed in the WAXS sample holder so that the liquid remained under the film, transported to the device within 15 minutes in a Petri dish containing liquid ethylbenzene to suppress evaporation/desorption, WAXS pattern measured under ambient conditions followed by drying on air for 1 hour. *iii*) The same as *ii*) but *o*-xylene was used. *iv*) The same as *ii*) but a mixture of *o*-xylene/ethylbenzene 1/1 by mass was used. *v*) The same as *ii*) but *p*-xylene was used. *vi*) The same as *ii*) but *m*-xylene was used. Although the WAXS patterns were measured with care for swollen films in steps *ii*) to *vi*), qualitative rather than quantitative information is provided by the patterns due to partial evaporation/desorption from the sample one-side exposed to the atmosphere, sample deformation, and temperature change during the scan. Part of the liquid was found to remain under the film after the WAXS scan.

RESULTS AND DISCUSSION

Sorption of single components in Matrimid® films

Sorption of ethylbenzene, *o*-, *m*-, *p*-xylene vapors was measured for Matrimid® films with the thickness of (50 ± 4) μm. The time required to reach apparent equilibrium followed the order: *o*-xylene >> *m*-xylene ≈ ethylbenzene > *p*-xylene. Anomalous diffusion was observed as the relative sorption deviated from proportionality to $\tau^{0.5}$ at small times, i.e. clear bend-up in the kinetics for *p*-xylene, *m*-xylene, and ethylbenzene occurred at the onset time (Fig. 2R). Due to the slow kinetics, measurements with *o*-xylene vapor sorption were discontinued, and the onset was not observed. The sorption isotherms for the remaining vapors were upward-curved and were well parameterized using the ABC isotherm [Eq. (2)]. The sorption uptakes for the liquids appeared higher (1.3 times for *m*- and *p*-xylene, 1.2 times for ethylbenzene) than those extrapolated from the data for the vapors (Fig. 2L, Table 1). These factors presumably correspond to the change of the specific surface of the polymer due to the more extensive swelling in the liquids - *A* presumably changed due to the polymer relaxation.

Kinetics for the sorption of the liquids was quicker (Fig. 2R) despite being measured with a thicker sample (103 ± 7) µm. This enabled the rough estimation of the diffusivity in the Matrimid® film for the sorption from the liquids using Eq. (1), $D_{o\text{-xylene}} \approx 2 \cdot 10^{-14}$ m^2s^{-1}, $D_{\text{ethylbenzene}} \approx 6 \cdot 10^{-14}$ m^2s^{-1}. The sorption uptakes for the single-component liquids followed the order *o*-xylene >> *p*-xylene > *m*-xylene > ethylbenzene. Differences in sorbate size and isomer specificity of van der Waals interactions with the polymer are expected. High adsorption of *o*-xylene has previously been reported for several metal–organic frameworks [3, 37-40], which was attributed to the van der Waals interactions and supposedly applies also to Matrimid®.

By considering the linear combination of the specific surface excesses of pure compounds (ethylbenzene/*o*-xylene/*m*-xylene/*p*-xylene, ratios 0.33/1/2/1), the hypothetical specific surface excesses yield 0.528 g g^{-1}. By using the density [41] of Matrimid® of 1.238 g cm^{-3}, then the approximate total xylene capacity of 6.15 mmol cm^{-3} is obtained, which is rather high. The total xylene capacity of most Metal-Organic Frameworks is below 7 mmol cm^{-3} for a selection of 2500 MOFs [42] and for common industrial adsorbents [3]. From the application perspective, the desorption of Matrimid® by methanol is unusual, while the industrial adsorbents are desorbed by toluene, paradiethylbenzene, ethylbenzene, etc. [10, 43]. Nevertheless, methanol does not form an azeotrope with *m*-xylene at 95 kPa [44], which supports the potential applicability of Matrimid® for the *o*-xylene recovery or removal.

The sizes of the studied sorbates can be defined by the minimum size of the slit (MIN-1) and elliptic cylindrical (MIN-2; MIN-1) pore needed to accommodate the molecule [45]. Expressed in nanometers, (MIN-1; MIN-2) equals (0.3834; 0.7269) for *o*-xylene, (0.3949; 0.7258) for *m*-xylene, (0.3810; 0.6618) for *p*-xylene, and (0.5285; 0.6625) for ethylbenzene. The pronounced difference in the vapor sorption kinetics for similarly sized *o*-xylene and *m*-xylene indicates the isomer-specificity of the van der Waals interactions. The material expectedly contains both types of assumed pores as the change of each parameter (MIN-1 and MIN-2) influences the vapor sorption kinetics including the onset of the non-Fickian behavior (compare pairs *p*-xylene and ethylbenzene, *p*-xylene and *o*-xylene).

Table 1. ABC parameters for sorption of single-component vapors and liquids in Matrimid® films at 35.0 °C were determined using Eq. (2), zero B and C were set for the liquids. Note that all pure-component sorbates are labeled by index 2 in this work.

Sorbate, pure compound 2	A_2^{vap}, g g^{-1}	A_2^{liq}, g g^{-1}	B_2^{vap}, g g^{-1}	C_2^{vap}, g g^{-1}
m-xylene	0.297	2.00	-4.11	3.62
p-xylene	0.444	1.86	-3.60	3.27
Ethylbenzene	0.604	2.05	-3.41	3.21
o-xylene	N/A	1.74	N/A	N/A

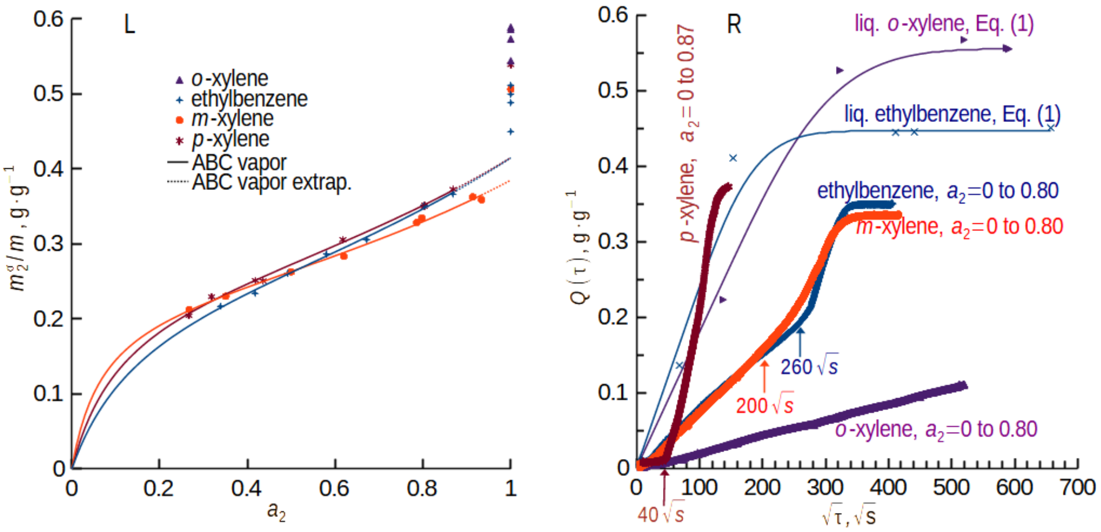

Fig. 2. Single-component vapor and liquid sorption isotherms (L) and kinetics expressed as total sorbate mass in the film per its mass (R), unit activity means pure liquid sorptive while Poynting correction corresponding to the pressure change from the saturated vapor pressure to atmospheric was neglected. All data are for 35.0 °C, at which kinetics and sorption isotherms for vapors were measured with Matrimid® films (50 ± 4) μm, liquid sorption uptakes and kinetics with films (103 ± 7) μm. Points are experimental, curves represent Eq. (2) and Eq. (1) in L and R, respectively. The onset of the non-Fickian behavior is indicated in R. Note that all pure-component sorbates are labeled by index 2 in this work, and that only experimental points are shown for the vapor sorption kinetics. Data are in SD.

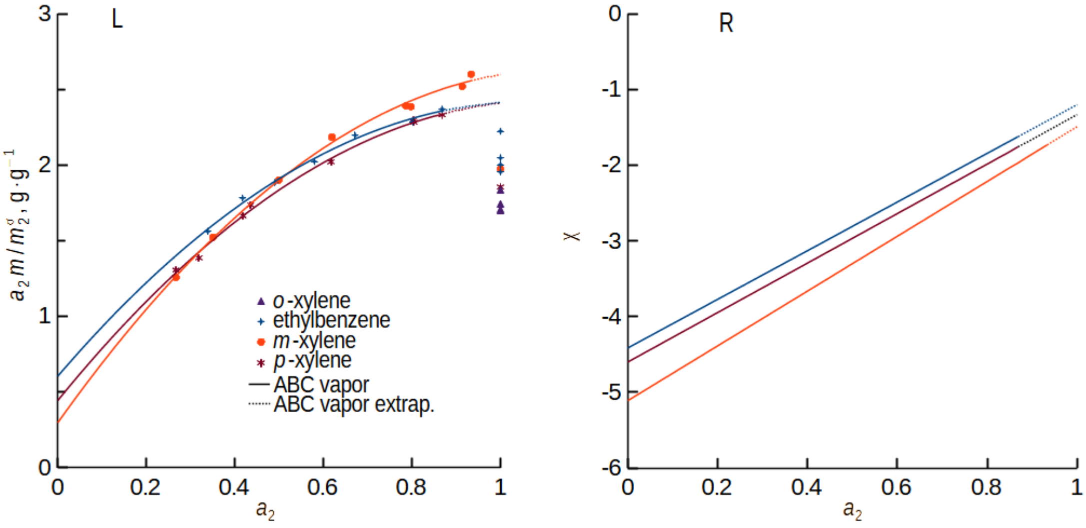

Fig. 3. Plot of $a_2 m/m_2^g$ versus a_2 (L) and plot of χ versus a_2 calculated using Eq. (3) (R). Curves are derived based on the ABC model [Eqs. (2,3)] with parameters calculated for sorption of vapors in Matrimid® films at 35.0 °C listed in Table 1. Experimental data for single-component vapors and liquids ($a_2 = 1$) are shown. Note that all pure-component sorbates are labeled by index 2 in this work.

Sorption of liquid mixtures in Matrimid® films

Sorption of equimolar liquid mixture of ethylbenzene, *o*-, *m*-, *p*-xylene in Matrimid® led to the following separation factors for the respective (incl. redundant) pairs: *S*(*o*-xylene/ethylbenzene) = 1.16, *S*(*o*-xylene/ *m*-xylene) = 1.07, *S*(*o*-xylene/*p*-xylene) = 1.08, *S*(*m*-xylene/*p*-xylene) = 1.01, *S*(*p*-xylene/ethylbenzene) = 1.08, *S*(ethylbenzene/*m*-xylene) = 1.09, which is consistent with the observed uptakes for the single-component liquids. Sorption of the liquid mixtures of *o*-xylene and ethylbenzene in Matrimid® films was thus studied in detail for two independent samples subjected to different series of experiments and varied incubation times (details are in SD). The samples became subjectively stiffer after the series of sorption measurements with no detected weight losses. The composite isotherm (Fig. 4L) and relative specific surface excess (Fig. 5) revealed no sorption competitiveness and good measurement repeatability. The specific surface excess was proportional for *o*-xylene and ethylbenzene over the entire concentration range (Fig. 4R). This implies negligible parameters *B* and *C* for the sorption of the two-component liquids, the same is assumed for the single-component liquids, as all four studied compounds are similar (constitutional isomers). This signifies that sorption was dominated by sorbate-surface interaction with the sorbent (i.e., the mono sorbate-surface term, A^{-1}). We emphasize that the parameter $A_i^{\text{liq,mix}}$ in Eq. (2) calculated from the measured data for the sorption of liquid mixtures equaled the A_i^{liq} calculated from the data on the sorption of pure liquids within the experimental uncertainty (the former is in Fig. 4R, the latter in Table 1), which paves the way to an elucidation of sorptive-sorbent interactions through the swelling measurements. Matrimid® contains moieties with affinity to *o*-xylene over ethylbenzene as different values of $A_i^{\mathrm{liq,mix}}$ were observed (Fig. 4R), while attractive forces compensated the repulsion for the swelling in the binary liquids. The ramification for the negligible B and C comes from Eq. (3), see also Fig. 4. Derivative of a constant occurs on the left-hand side of Eq. (8) for the studied system:

$$\frac{\partial}{\partial a_2}\frac{a_2}{\frac{m_2^{\sigma(1)}}{m}} = \frac{\partial}{\partial a_2}A_2^{\mathrm{rel}} = 0\ \mathrm{g\ g}^{-1} \tag{9}$$

Furthermore, the separation factor simplifies to a constant independent of the bulk liquid composition (Fig. 4R, Fig. 6L). From Eqs. (2,6,8,9) we get

$$S^2 = \left(\frac{A_1^{\mathrm{liq,mix}}}{A_2^{\mathrm{liq,mix}}}\right)^2 = (1.19 \pm 0.05)^2 = \frac{\chi^{\mathrm{liq}}+1}{\chi^{\sigma}+1} \tag{10}$$

which means that the presence of Matrimid® weakens the sorbate-sorbate interaction slightly as compared to the bulk solution. The balance between a slightly favorable attraction ($S > 1$) and a slightly weakened sorbate-sorbate interaction balances out to form a linear sorption isotherm (Fig. 4).

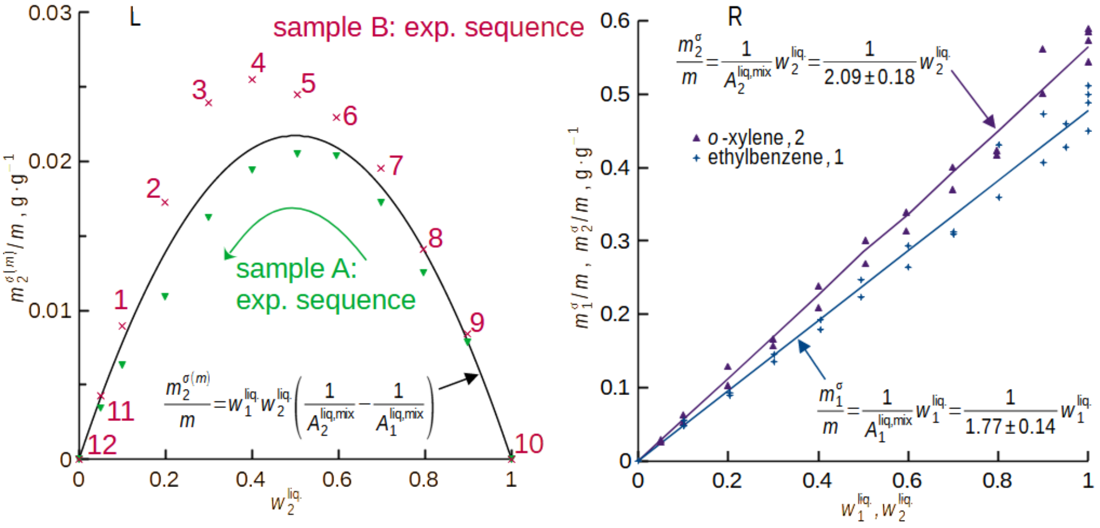

Fig. 4. Specific reduced surface excess (composite isotherm) (L) and specific surface excess (R) are shown for the indicated liquids and Matrimid® film at 35.0 °C. Curves represent Eqs. (2,5), in which $B_2^{\mathrm{liq,mix}} = C_2^{\mathrm{liq,mix}} = 0$ g g^{-1}. Data were collected for two independent samples [film thicknesses were 103 ± 7 um (A), 46 ± 4 um (B)], the measuring sequence is indicated (L), see SD for data and details.

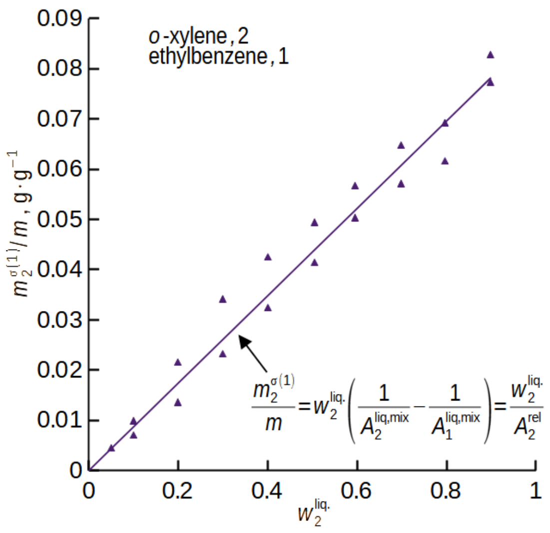

Fig. 5. Specific relative surface excess for the indicated liquids and Matrimid® film at 35.0 °C. Curves represent Eq. (4), in which $B_2^{\text{liq,mix}} = C_2^{\text{liq,mix}} = 0$ g g^{-1}. Data are in SD.

The sorption of the liquid mixtures of *o*-xylene and ethylbenzene in Matrimid® films can be viewed as *o*-xylene extraction from the liquid into Matrimid®. Consistent with previous findings, both the separation factor and the activity coefficients of *o*-xylene and ethylbenzene in Matrimid® remained constant (Fig. 6), calculation of the Nernst distribution coefficient is straightforward. This constancy of activity coefficients implies that the single-component sorbate in Matrimid® is not in the standard state of pure liquid, no sign of convergence to unity for the pure compounds was discerned.

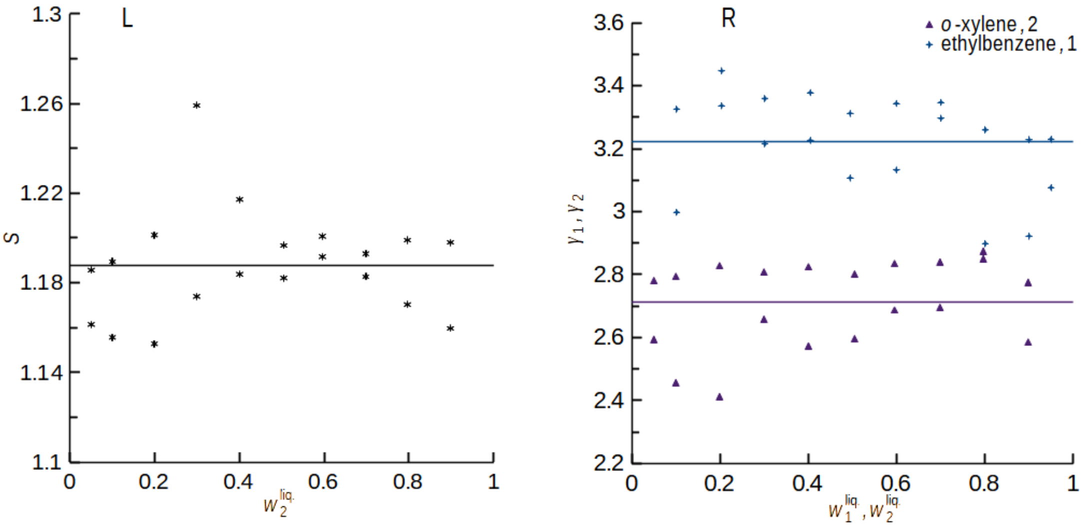

Fig. 6. Separation factor (L) and activity coefficients (R) for the binary sorbate in Matrimid® at 35.0 °C. Lines indicate averages, which are $S = 1.19 \pm 0.05$, $\gamma_{\mathrm{ethylbenzene}} = 3.2 \pm 0.3$, $\gamma_{o\text{-xylene}} = 2.7 \pm 0.3$. Data are in SD.

WAXS

The WAXS pattern of pure methanol-soaked vacuum-dried Matrimid® film indicates the amorphous nature and conforms to previous reports [31, 46], three broad bands were discerned at $2\theta \approx 16.0$ °; 23.5 °; 45.0 °. The pattern of the film changed upon its swelling in liquid ethylbenzene, *o*-xylene, and *o*-xylene/ethylbenzene (1/1), *p*-xylene, and *m*-xylene. A shift of the main Matrimid® band from 16.0 ° to 16.8 ° and intensity decrease due to swelling corresponds to the loosening of less stable domains. The *d*-spacing (Bragg's law) of the two (more) stable domains (16.8 °, 23.5 °) well corresponded to the minimum sizes of slit pores (MIN-1, Fig. 7) needed to accommodate ethylbenzene and *o*-xylene. Similar patterns were observed for Matrimid® swollen in the compounds of similar MIN-2 (*o*-xylene and *m*-xylene pair, ethylbenzene and *p*-xylene pair). Two isomers having very similar MIN-1 and MIN-2 (*o*-xylene and *m*-xylene) not only showed similar patterns but also a clear intensity shift. The higher sorption of *o*-xylene can thus be accounted for the isomer-specific van der Waals interactions. Deepening the understanding of these interactions, such as using dielectric spectroscopy measurements [47], are foreseen. Overall, Matrimid® contains harder (sorbate resistant) and softer domains, free volume voids are essentially of two types (slit, elliptic cylindrical pores), and specific sorbate-polymer interactions are expectable as different WAXS patterns are observed for isomers of the same size.

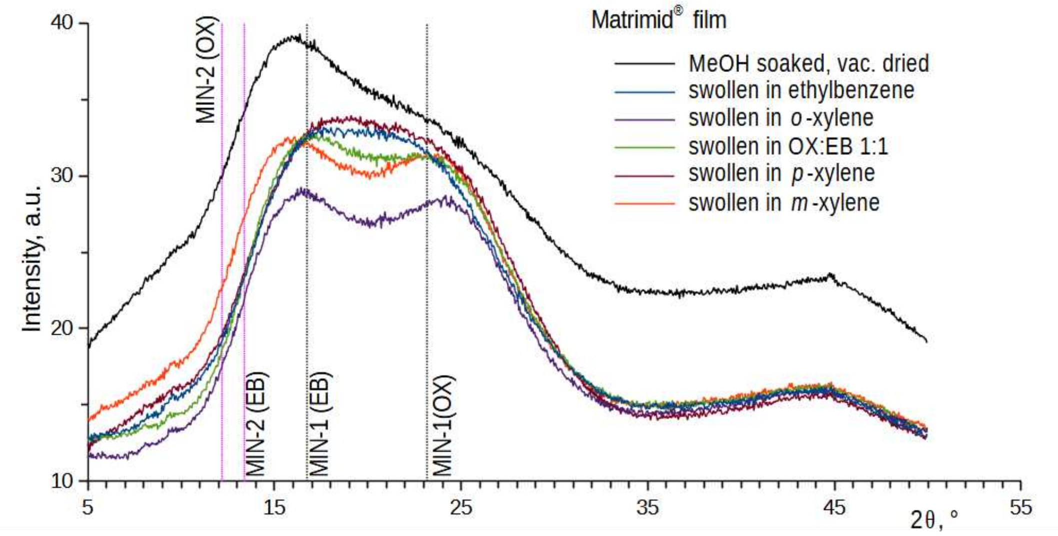

Fig. 7. WAXS patterns for Matrimid® film (120 ± 5) μm thick that was methanol-soaked vacuum-dried, exposed to liquid ethylbenzene, *o*-xylene, *o*-xylene/ethylbenzene (1/1), *p*-xylene, and *m*-xylene. MIN-1 and MIN-2 are minimum of slit and elliptic cylindrical pore sizes to accommodate the molecule [45]. Data are in SD.

CONCLUSION

Dense films from Matrimid® showed sorption uptakes of single-component liquids following the order *o*-xylene > *p*-xylene > *m*-xylene ≈ ethylbenzene. Vapor sorption isotherms for the pure sorptives followed the ABC model, which can capture the dual character of sorption-dissolution without any overly idealized assumptions (such as layer-by-layer adsorption on a homogeneous surface). All three contributions (mono-, di-, tri-sorbate interactions with sorbent, A^{-1}, B, and C) were necessary to fit the vapor sorption data, kinetics corresponded to the non-Fickian diffusion with relaxation. For the sorption from the binary mixtures (*o*-xylene, ethylbenzene), only the sorbate-surface interaction (i.e., the mono term, A) with the sorbent sufficed to parameterize the sorption data presumably due to excessive polymer relaxation in the liquid, which was demonstrated to be consistent with the estimation of A from single-component liquids. Importantly, the same constant A described sorption from both single- and two-component liquids, which is not the theoretically predicted behavior, follow-up model development is foreseen. Separation factors observed for the equimolar quaternary liquid mixtures of *o*-xylene, *p*-xylene, *m*-xylene, and ethylbenzene showed that Matrimid® is most selective for *o*-xylene over ethylbenzene. The separation factor was constant (1.19 ± 0.05) irrespective of the liquid composition for the sorption of the binary liquid mixtures. The linear sorption isotherms for the liquid mixtures and the selectivity of Matrimid® to *o*-xylene over ethylbenzene imply that the sorbate-sorbate interaction is weakened slightly as compared to the bulk solution of these two compounds. This study fosters the use of glassy polymers as sorbates, which can undergo profound changes due to the swelling in the environment, but which does not avoid sorption preferentiality. Moreover, a new technique for the measurement of sorption of liquid mixtures in dense polymer films was demonstrated on Matrimid®, which is a polymer glass showing entrapment of volatile compounds. In the future, polymer optimization is foreseen to reach polymers enabling the recovery of the highly valuable *p*-xylene from its mixtures with other C_8H_{10} compounds, chiefly *m*-xylene, or breaking of other hard-to-separate mixtures.

ACKNOWLEDGEMENT

The authors thank Jan Heyda for inspirational discussion, Petr Sysel for the provision of raw Matrimid®, Martina Kohoutková and Jaroslav Maixner for the WAXS analyses. JS acknowledges the support obtained from The Ministry of Education, Youth and Sports within the specific university research grants A1_FCHI_2024_001, A1_FCHI_2025_001.

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