

Sorption Isotherms of Organic Vapors on Polyurethane Foams

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Received: April 2, 2004; In Final Form: July 1, 2004

The sorption of toluene at 25 °C in different polyurethane foams was studied. The results revealed that the differences in the composition of the foams have only a small influence in the sorption capacity, indicating that the sorption is mainly controlled by dispersion forces. The sorption isotherms of benzene, toluene, ethylbenzene, cyclohexane, and methyl ethyl ketone (MEK) at 25, 30, and 35 °C were determined in a selected polyurethane foam. The three-suffix Margules equation and the Flory–Huggins equation were used to correlate the experimental data of the aromatic compounds at different temperatures. The prediction of the sorption isotherms of cyclohexane and MEK at different temperatures was attempted with the Flory–Huggins equation. The predicted sorption isotherms of cyclohexane were similar to those obtained by the interpolation with the Margules equation. However, for the MEK, the prediction is rather poor, due probably to the high dipole moment of this molecule. The validity of the estimations at low pressures was discussed by comparison of the predicted activity coefficients at infinite dilution, obtained by the two methods, with the ones obtained from the Henry's law.

Introduction

The application of polyurethane foams in air-filtering systems is based on the ability of these materials to physically retain small particles in their reticulated and tortuous open cell structure. On the other hand, the use of adsorbent materials in the purification of gas streams is a well established technology, and their principles are reasonably understood.^{1,2} However, the adsorbent materials are usually obtained in powder or in a granular form, which in many cases constrains their use. The feasibility of the inclusion of adsorbent materials in polyurethane foams, to obtain composite materials with adsorption capabilities, was recently demonstrated.³ Nevertheless, many aspects of these new composite materials require a detailed study, especially when specific applications to air-filtering systems are envisaged.

The main advantage of these new composite materials could be the application to adsorb organic vapors and increase the indoor air quality. The modeling of the sorption of organic vapors in the composite materials requires the knowledge of their sorption behavior on each component (polymer and adsorbent). In this work, the interaction of some organic vapors with the polymeric matrix used as adsorbent support is studied. The interaction of toluene vapor with polyurethane foams of different compositions and the sorption of several solvents, toluene, benzene, ethylbenzene, cyclohexane, and methylethylketone (MEK), in a selected foam are discussed. In the present study, toluene was selected as a probe molecule since it is a relatively common pollutant and can be seen as representative of the large family of aromatic volatile compounds.

A question of major importance in the application of the composite materials is the prediction of the amounts of different vapors that can be sorbed in the polymeric matrix. Two methodologies were applied in the analysis of the sorption isotherms, based in the prediction of the activity coefficients of the vapor in the polymeric matrix. The first uses the three-suffix Margules equation⁴ and can only be applied to the prediction of isotherms of one vapor. The second is based in the theory of Flory–Huggins for polymer solutions⁵ and has the advantage over the Margules equation that it can be generalized to the prediction of sorption isotherms of different vapors since the estimated parameters are characteristic of the components of the mixture. The two methodologies can be applied to the vapor/polymer equilibrium by calculating the fugacity of the vapor in the vapor phase.

A large number of theories and equations have been proposed by several authors for the estimation of properties of polymer solutions, and many, but not all, are based in the lattice theory of Guggenheim.^{6,7} A short time after Flory and Huggins presented their works, Zimm⁸ proposed a statistical mechanics approach that was later developed by other authors.^{9,10} More recently, some authors proposed changes to the original Flory–Huggins assumptions that try to account for the possibility of the nonrandomness of the mixture.^{11–14} Different methods for the estimation of properties of polymer solutions have been reviewed and applied by several authors, many of them based in models of hard spheres chains,^{15–17} in computer simulations by Monte Carlo methods¹⁸ or using density functional theory methods,¹⁹ and in group contribution methods.^{20,21} However, the majority of these methods require some knowledge of the polymer structure and/or detailed chemical composition for their application and, in more simple cases, such as for example polyethylene, polypropylene, polystyrene, and polydimethylsiloxane, a good prediction can be achieved.^{20,21} In the case of

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the polyurethane foams used in a very large number of industrial and technological applications, the cross-linking density, molecular weight, and detailed chemical composition are not completely known and often cannot be easily determined. Thus, the methods mentioned above cannot be directly applied to the majority of polyurethane foams, and the same situation occurs for the application to other technologically important polymers.

In this work, a simple and relatively straightforward method for the estimation of sorption isotherms at room temperature is presented. Although essentially empirical, it can be applied in principle to any polymer/vapor system. It has also the advantage of being of simpler calculation in contrast with many of the other methods mentioned above.

Theoretical Models

The fugacity of component i sorbed in the polymer can be estimated from the fugacity of the vapor phase, since at equilibrium^{7,22}

$$f_i^s = f_i^v \quad (1)$$

were f_i^s and f_i^v are the fugacity of component i sorbed in the polymer and in the vapor phase, respectively. If we consider a system of two components and only one can be in the vapor phase, as is the case in the vapor/polymer system, the pressure of the system is the partial pressure of the organic vapor. Thus, introducing the fugacity coefficients of the vapor at pressure p and at saturation pressure p° , represented by φ and φ° , respectively, eq 1 can be rearranged for calculating the activity coefficient of the vapor in the polymer γ_2

$$\gamma_2 = \frac{p\varphi}{x_2 p^\circ \varphi^\circ} \quad (2)$$

where x_2 is the concentration of the vapor in the mixture (polymer and solvent). For convenience in the calculations, x_2 can be expressed in mass fraction (mass of vapor/mass of mixture) since $x_2 \rightarrow 1$ as $p \rightarrow p^\circ$. However, experimentally, the values are normally determined per mass of clean solid. The amounts sorbed n^s , expressed per mass of clean solid are related to x_2 by

$$n^s = \frac{x_2}{M_2(1 - x_2)} \quad (3)$$

where M_2 is the molar mass of the vapor. In this work, the values of x_2 were determined directly by the gravimetric method and their values were used in the following described equations. The application of eq 2 to estimate the activity coefficients requires that φ and φ° are known. The fugacity coefficients (φ , φ°) were calculated by the virial equation of state, truncated in the second virial coefficient. A generalized correlation proposed by Pitzer and Schreiber²³ for estimating the second virial coefficient at different temperatures was used, except for MEK, for which we used tabulated values.²⁴ Then, from sorption isotherms, the activity coefficients at different pressures and compositions can be estimated using eq 2.

The correlation of γ_2 with composition and temperature would be of interest since it would allow the calculation of p at a given x_2 and consequently the estimation of sorption isotherms at different temperatures.

The three-suffix Margules equation is often used to represent experimentally determined activity coefficients, in which A and

B are normally obtained by fitting the equation to experimental data²⁵

$$RT \ln \gamma_2 = (A - 3B)(1 - x_2)^2 + 4B(1 - x_2)^3 \quad (4)$$

Although the A and B parameters could have to some extent a physical significance, in the majority of cases, eq 4 is used in an empirical basis for the interpolation and extrapolation of experimental data.^{4,25} Equation 4 has been widely applied to vapor–liquid equilibrium data, giving normally a good description of the experimental data.

A theory developed for polymers in solution was proposed by Flory²⁶ and Huggins²⁷ and was first applied by Prager, Bagley, and Long²⁸ to the equilibrium of different vapors in polyisobutylene. Briefly, the Flory–Huggins theory states that γ_2 can be represented as a function of the volume fraction occupied by the polymer in the mixture Φ_1 by⁵

$$\ln \gamma_2 = \ln \left[1 - \left(1 - \frac{1}{r} \right) \Phi_1 \right] + \left(1 - \frac{1}{r} \right) \Phi_1 + \chi \Phi_1^2 \quad (5)$$

where r is the number of segments in a polymer molecule and is usually chosen in order to represent the number of solvent molecules per polymer chain (coordination number). The interaction parameter χ is determined by intermolecular forces and according to the theory should be independent of polymer concentration and of polymer molecular weight, but in many systems, a slight dependence is observed. The parameter χ can be related to the Scatchard–Hildebrand theory by⁴

$$\chi = \frac{v_2}{RT} (\delta_2 - \delta_1)^2 \quad (6)$$

where δ_1 and δ_2 are solubility parameters of polymer and solvent, respectively, also called cohesive energy density, which were determined for a large number of solvents,^{29,30} R is the perfect gas constant and v_2 is the molar volume of the solvent. The application of the eq 5 requires also the calculation of Φ_1 that can be achieved by^{4,5}

$$\Phi_1 = \frac{x_1 v_{sp1}}{x_1 v_{sp1} + x_2 v_{sp2}} \quad (7)$$

were v_{sp1} and v_{sp2} are the specific volumes of the polymer and the solvent (in the liquid state), respectively. Usually eq 5 is used in the determination of χ by fitting to experimental data.⁵ The usual approach of adjusting only Φ_1 for each polymer/vapor system (considering $\chi = 0$) could not correlate our data and could not be extended to the prediction of sorption isotherms in other polymer/vapor systems. In this work, we considered r , δ_1 , and v_{sp1} as empirically adjustable parameters for a given polyurethane matrix and characteristic of the polyurethane. These values could then be applied in the estimation of sorption isotherms for two other vapors (cyclohexane and MEK), and a comparison of the differences with experimental data was made.

Experimental Section

The sorption isotherms were determined by the gravimetric method in a balance (Disbal, C. I. Electronics) suited for vacuum. The samples of polyurethane foams were outgassed by heating at 50 °C in a vacuum better than 10^{-2} Pa for 2.5 h. The vapor was then introduced in the system and allowed to equilibrate with the sample. Pressure readings were made in a capacitance transducer (CMR 262, Piffer Vacuum). The tem-

TABLE 1: Composition of the Two Series of Formulations

component	formulation series	
	A	B
type	TDI	MDI
isocyanate		
NCO index (%)	105	105
polyol (g)	20.00	20.00
dibutyltin dilaurate (g)	0.23	0.23
silicone Oil (g)	0.40	0.40
water content (%) ^a	1–5.5	3–4

^a Percent in polyol weight.

perature was controlled using a water bath (GD120, Grant), with 0.05 °C precision.

The vapors used were benzene (Riedel-de Haën, <99.5%), toluene (Aldrich, <99.5%), ethylbenzene (Aldrich, 99%), cyclohexane (Merck, 99.9%), and MEK (BDH, 99%). All were purified in situ by freeze–vacuum–thaw cycles.

The synthesis and characterization of the polyurethane foams used were described with detail elsewhere.³ Briefly, the required quantities of polyol, distilled water, silicone oil, and catalyst were added in a polyethylene flask and mixed vigorously during 1 min with a mechanical stirrer, to obtain the formulated polyol. The isocyanate was then added to the same flask, and a strong stirring was applied during 15 ± 2 s. The resulting mixture was left undisturbed for 1 min, allowing the formation and growth of the foam, and was immediately introduced and kept in an oven at 70 ± 1 °C during 1 h. The samples used were synthesized with methylene bisphenyl diisocyanate (MDI) or toluene diisocyanate (TDI) and different water contents in the formulation. Except for isocyanate which was adjusted to 105% NCO index in all the formulations, the other components were maintained constant, as can be observed in Table 1.

The formulated polyol was a mixture of 20 g of 1,2,3-tris-(polyoxypropylene ether)propane (Aldrich, number-average molecular weight ≈ 3600 , 41 mg KOH g⁻¹), 0.23 g of dibutyltin dilaurate (Merck, >97%), 0.40 g of silicone oil (Dow Corning, 193 Surfactant), and water (different amounts were used along each series, see Table 1). The isocyanates were MDI (BASF, Lupan M 50) and TDI (Aldrich, 80% of the 2,4 isomer and 20% of the 2,6 isomer). To maintain the 105% NCO index in each formulation series, the amount of isocyanate were changed accordingly.

The apparent specific gravity of the foams was between 110 and 27 kg m⁻³ for the TDI series and between 33 and 59 kg m⁻³ for the MDI series.³ All the samples had an open cell volume between 89 and 98%, determined by gas pycnometry.³

The sorption of toluene was made in all the synthesized samples, at 25 °C. The sorption of the other vapors was made in a selected sample synthesized with MDI and with 3.85% water content in the formulation, at 25, 30, and 35 °C. This foam was selected in a previous work³ since it presented desired characteristics to be used as a matrix for supporting granular adsorbent materials as, for instance, activated carbons.

Results and Discussion

The sorption isotherms of toluene in the polyurethane samples are presented in Figure 1. All the samples present similar sorbed amounts, and the shape of the isotherms are also very similar. Also, the sorption of toluene was reversible in all samples. Only at high relative pressures (p/p°) did the sorbed amounts become significant, which indicates a weak interaction between the toluene molecule and the polymeric matrixes. However, the small differences shown among the samples of the same

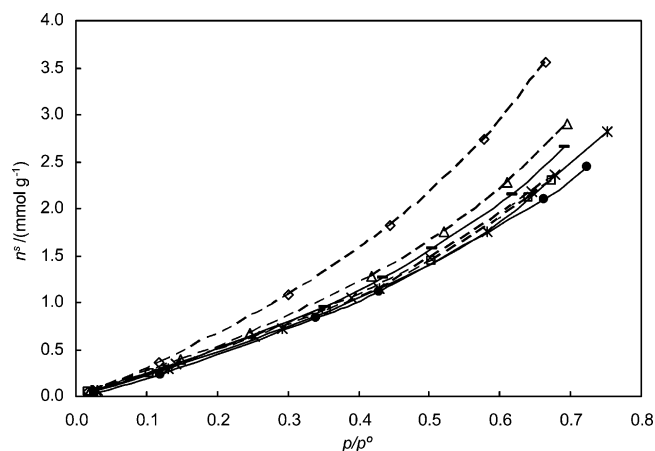


Figure 1. Sorption isotherms of toluene at 25 °C in different samples of polyurethane foams. Broken and solid lines represent isotherms of foams from series A and B, respectively. Symbols for foams with the water content in the formulation as follows: from series A, \square 5.5%, \times 4.5%, \triangle 2.5%, \diamond 1%; from series B, \bullet 4%, $*$ 3.9%, $-$ 3%.

formulation series can be rationalized since in the samples synthesized with high water contents present low sorption capacities. That is, in each formulation series, there is a high affinity of toluene for samples synthesized with less water contents.

This result is in accordance with the water isotherms determined on these foams.³ The more hydrophobic samples were synthesized with less water in the formulation and presented higher sorption capacities for toluene. The samples synthesized with more water have more urea groups in their polymeric matrix, which are polar groups. Probably the interaction of toluene, a nonpolar molecule, with matrixes with a higher quantity of polar groups in their constitution is less effective. Therefore, the more hydrophobic samples, which have less quantity of polar groups, present high sorption capacities of toluene. This type of relation has also been described for other polymers.^{31,32}

These observations are in line with what was stated above with respect to the differences in the toluene isotherms, among the samples of the same formulation series. However, the small differences encountered between all the samples presented in Figure 1 indicate that the interaction of the toluene vapor with the polyurethane matrix is mainly controlled by dispersion forces and that the effect of the dipoles in the polymeric matrixes is not the dominant factor. Although a possible influence of the cross-linking of the polymer could be present in the differences in the sorption isotherms among the samples of each formulation series, this seems not to be clear from the experimental results. In fact, it is expected that the cross-linking increases more with the water content in the case of the MDI series (series B) than in the case of the TDI (series A), due to the higher functionality of the MDI, but the variation in sorption isotherms along each series are very similar.

The sorption of benzene, toluene, ethylbenzene, cyclohexane, and MEK vapors was made in a selected sample of polyurethane foam synthesized with MDI and 3.85% water content. The sorption isotherms obtained at 25, 30, and 35 °C, in the form of n^s vs p , are presented in Figures 2–6 and all were reversible. It was observed by comparison of these figures with plots of n^s vs p/p° (see Figures 3 and 7, for instance) that for each vapor that the main effect of the temperature in the isotherms is through the differences in saturation pressure (p°) at each temperature. When the results are expressed in relative pressure

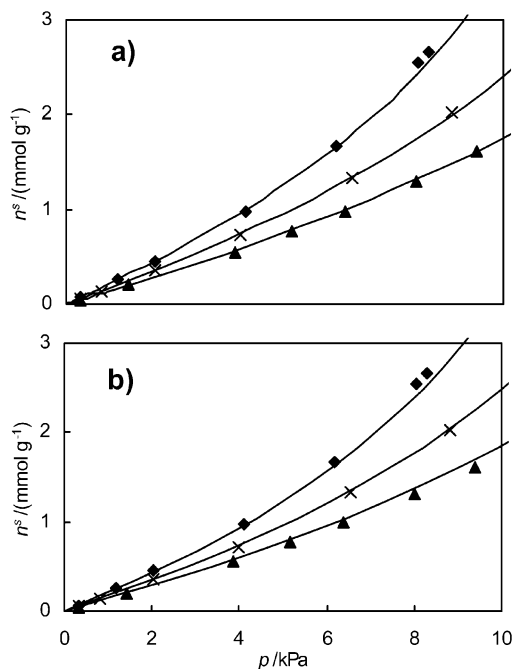


Figure 2. Sorption isotherms of benzene on the selected polyurethane foam (see text) at: \blacklozenge 25 °C, \times 30 °C, \blacktriangle 35 °C. (a) Lines represent the fit of the three-suffix Margules equation. (b) Lines represent the fit of the Flory–Huggins equation.

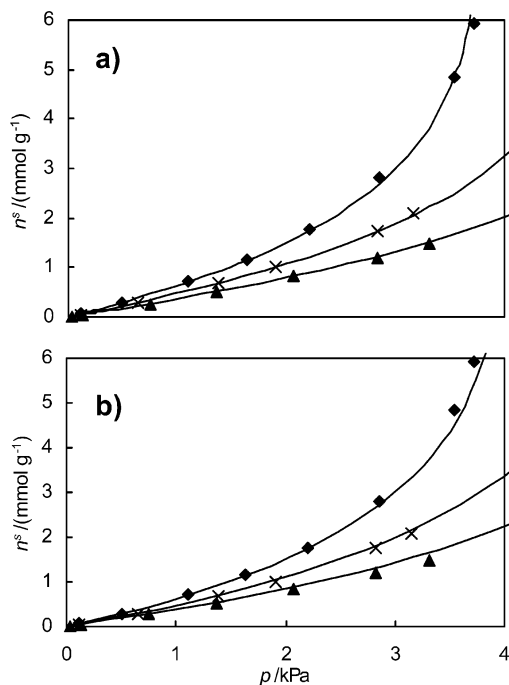


Figure 3. Sorption isotherms of toluene on the selected polyurethane foam (see text) at: \blacklozenge 25 °C, \times 30 °C, \blacktriangle 35 °C. (a) Lines represent the fit of the three-suffix Margules equation. (b) Lines represent the fit of the Flory–Huggins equation.

(p/p°), the differences in the isotherms, at different temperatures, almost vanish for each vapor, as can be seen in the example of Figure 7.

For the aromatic compounds, it can also be observed that the polyurethane foam has slightly high sorption amounts for the more volatile at the same p/p° . This means that the affinity of the polyurethane follows the order benzene > toluene > ethylbenzene. However, cyclohexane and MEK, which have saturation pressures similar to those of benzene, present different sorption amounts. The cyclohexane presents the highest sorption

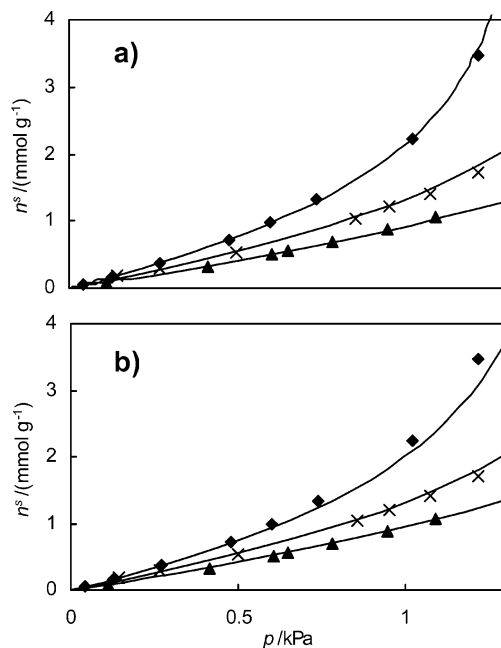


Figure 4. Sorption isotherms of ethylbenzene on the selected polyurethane foam (see text) at: \blacklozenge 25 °C, \times 30 °C, \blacktriangle 35 °C. (a) Lines represent the fit of the three-suffix Margules equation. (b) Lines represent the fit of the Flory–Huggins equation.

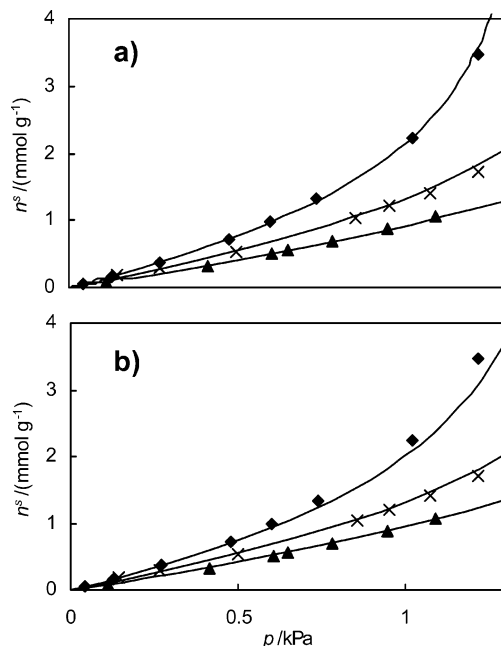


Figure 5. Sorption isotherms of cyclohexane on the selected polyurethane foam (see text) at: \blacklozenge 25 °C, \times 30 °C, \blacktriangle 35 °C. (a) Lines represent the fit of the three-suffix Margules equation. (b) Lines represent the fit of the Flory–Huggins equation.

amounts of all the vapors tested, and compared with benzene, this indicates that the polyurethane has a stronger affinity for the nonaromatic compound. The strong dipole moment of the MEK molecule could be the reason for the low amounts observed, bearing in mind what was stated above for the dependence of the sorption of toluene with the hydrophobicity of the foams.

The fitting of the three-suffix Margules equation was made to the isotherms of each vapor. An example of the representation of f/p° and $\ln \gamma_2$ as a function of x_2 is given in Figure 8 for benzene. The γ_2 and x_2 were calculated using eqs 2 and 3, respectively. For MEK, the strong nonideality of the gas-phase

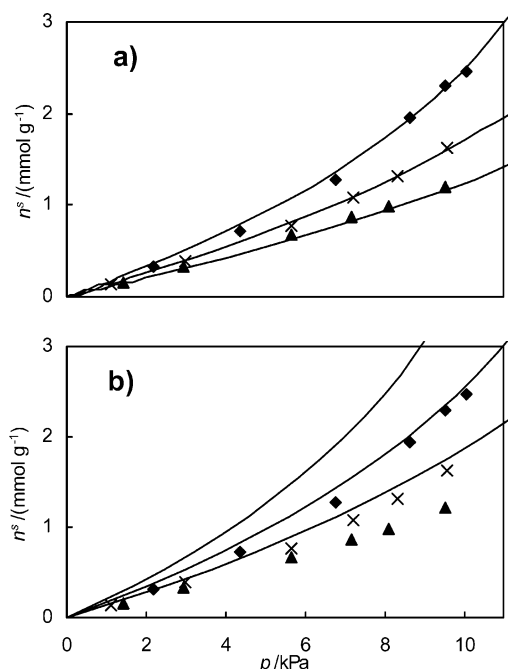


Figure 6. Sorption isotherms of MEK on the selected polyurethane foam (see text) at: \blacklozenge 25 °C, \times 30 °C, \blacktriangle 35 °C. (a) Lines represent the fit of the three-suffix Margules equation. (b) Lines represent the fit of the Flory–Huggins equation.

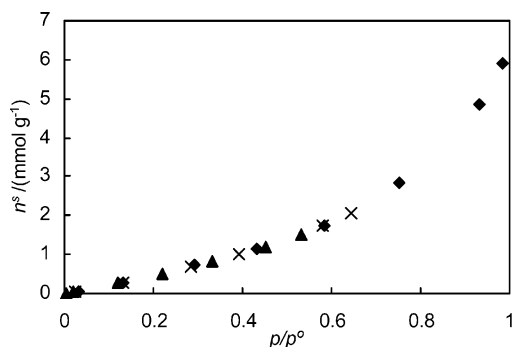


Figure 7. Sorption isotherms of toluene on the selected polyurethane foam (see text) at: \blacklozenge 25 °C, \times 30 °C, \blacktriangle 35 °C, represented as a function of p/p^o . For each temperature was considered a different value of p^o since it is a function of $T, p^o(T)$.

is responsible for a slight separation of the data of different temperatures. The fact that, for all the vapors, the data at different temperatures are almost indistinguishable in representations such as those of Figure 8 is an indication that the activity coefficient is not strongly temperature dependent. This fact supports the application of eq 4 to the data at three different temperatures together, considering an average temperature of 30 °C, estimating in this way one pair of constants, A and B , for each vapor. If this weak temperature dependence was not observed, a different set of constants for each temperature would be needed for the description of the experimental behavior. This approximation implies that A and B are considered temperature independent in the studied range and that the values estimated by the nonlinear least-squares fitting are presented in Table 2.

The values of A and B were then used to calculate $\ln \gamma_2$ as a function of x_2 , at an average temperature of 30 °C, and the values of p and n^s were then estimated using eqs 2 and 3, with the p^o value at the desired temperatures (25, 30, and 35 °C). The predicted isotherms are represented by the solid lines in Figures 2a–6a. Although based on the drastic assumption that γ_2 is temperature independent and on an essentially empirical

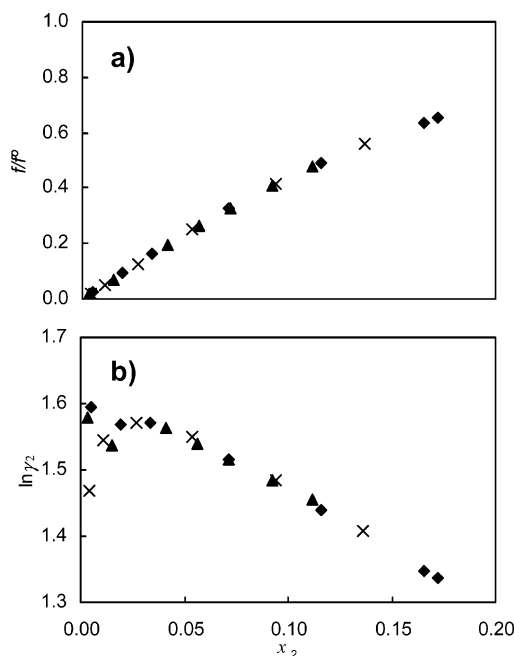


Figure 8. Representation of (a) fugacity and (b) activity coefficients of benzene, as a function of the concentration of the vapor on the selected polyurethane foam (see text).

TABLE 2: Estimated Parameters of the Three-Suffix Margules Equation for the Sorption Isotherms of the Different Vapors, at an Average Temperature of 30 °C, on the Selected Polyurethane Foam (See Text)

vapor	$A/(\text{kJ mol}^{-1})$	$B/(\text{kJ mol}^{-1})$
benzene	5.47	−1.50
toluene	5.52	−1.38
ethylbenzene	5.86	−1.39
cyclohexane	3.14	−0.82
MEK	6.54	−1.44

equation, the estimated values are very close to the experimental ones. The aromatic compounds present the more favorable situation with relative standard deviations (RSD) of 3.1, 4.4, and 6.3% between the experimental and the estimated values for the benzene, toluene, and ethylbenzene, respectively. For cyclohexane and MEK, the RSD were 10.5 and 5.7%, respectively. The relatively low RSD values give an indication of the validity of the approximation of temperature independence made in the estimation of A and B , in this temperature range. In this way, the parameters allow the estimation of sorption isotherms in this polyurethane sample from a simple two-parameter equation, between 25 and 35 °C, for each vapor. This approach can be used in principle to any other vapor and requires the experimental determination of only one isotherm (in the present case, preferably at 30 °C), to estimate the parameters A and B . Equation 4 could be replaced by a four-suffix Margules equation or by a more general Redlich–Kister expansion,⁴ if the data represented as in Figure 8 present a more complex variation with x_2 . However, in the presented cases (Figures 2a–6a), the simpler three-suffix Margules equation seems to be sufficient.

The extension of the prediction of sorption isotherms to other components was attempted using the Flory–Huggins equation (eq 5). This expression was adjusted to the data of the sorption isotherms of the aromatic compounds, at all temperatures, together in one data set. The only approximation done was to assume that $v_{\text{sp}1}$, $v_{\text{sp}2}$, δ_2 , and δ_1 were constant in this temperature range and equal to the value at 25 °C. The parameters used for the studied organic compounds³⁰ are presented in Table 3. The estimated parameters for the polymer,

TABLE 3: Properties of the Pure Liquid Organic Compounds Used in the Application of Eqs 6 and 7 at 25 °C³⁰

vapor	$\nu_{sp2}/(\text{cm}^3 \text{ g}^{-1})$	$\delta_2/(\text{J cm}^3)^{1/2}$
benzene	1.1445	18.8
toluene	1.1602	18.2
ethylbenzene	1.1585	18.0
cyclohexane	1.2916	16.8
MEK	1.2496	19.0

TABLE 4: Estimated Parameters of the Flory–Huggins Equation for the Selected Polyurethane Foam (See Text) from the Sorption Isotherms of Benzene, Toluene, and Ethylbenzene at 25, 30, and 35 °C

parameter	value
$\nu_{sp1}/(\text{cm}^3 \text{ g}^{-1})$	2.27
$\delta_1/(\text{J cm}^3)^{1/2}$	11.5
r	2.33

obtained by the nonlinear least-squares method, are presented in Table 4. The isotherms could then be predicted for the three compounds, at each temperature, and are represented by the solid lines in Figures 2b–4b. The RSD values of the prediction are 5.1, 4.3, and 6.8%, for benzene, toluene, and ethylbenzene, respectively. The comparison of these values with the RSD values obtained with the three-suffix Margules equation and also the comparison of parts a and b of Figures 2–4 show that similar results in the prediction of the sorption isotherms are obtained by the application of the Flory–Huggins equation. However, with this last equation, only three parameters need to be estimated to calculate the isotherms of the three organic vapors, in contrast with the two parameters for each organic vapor that needed to be estimated when using eq 4 (Table 2). Furthermore, contrary to the calculations made with the three-suffix Margules equation, the assumption that γ_2 is constant in the studied temperature range was not needed. The dependence of γ_2 with temperature was taken in to account in the calculations, specifically through the application of eq 6. These considerations show that the method based in the Flory–Huggins theory should be preferred in the prediction of the isotherms of the benzene, toluene, and ethylbenzene vapors in the polyurethane foam.

The application of the estimated parameters in Table 4 (obtained from the sorption of the aromatic compounds) to the prediction of the sorption isotherms of cyclohexane and MEK is presented in Figures 5b and 6b, and the corresponding relative standard deviation values are 14.6 and 26.4%. In the case of cyclohexane, the prediction is comparable to what was obtained with the Margules equation. However, it should be emphasized that, in this case, the isotherms of cyclohexane are entirely predicted from the parameters in Table 4, contrary to what is done with the Margules equation, where the equation is fitted to the adsorption data of cyclohexane. This result is a strong indication that the Flory–Huggins model can be applied successfully to the prediction of the cyclohexane adsorption in this polyurethane.

Through the other way, in the case of MEK, the prediction based in the Flory–Huggins equation is rather poor. This observation is probably related to the fact that eqs 5 and 6 are based on theories that assume complete randomness of mixing and do not take in to account the strong dipole moment of the MEK molecule (3.3 D).³³ In fact, this could explain the lower affinity of the MEK molecule to the polymeric matrix than what was predicted by the equation since the parameters used were estimated with nonpolar aromatic compounds that are very different from the strongly polar MEK. This is in line with what was stated above about the sorption of toluene in different

polyurethane foams and their relation to the hydrophobicity and chemical composition. The strong dipole of the MEK molecule could explain the low sorbed amounts in an essentially nonpolar polymeric matrix. From this, it is reasonable to assume that the prediction of sorption isotherms of polar molecules based in parameters estimated from sorption isotherms of nonpolar molecules can, in principle, overestimate the sorption amounts. Nevertheless, the reasonable prediction of the cyclohexane isotherms indicates that this methodology could be applied in the prediction of sorption isotherms of other nonpolar molecules.

Some considerations can be made about the values in Table 4; however, one should keep in mind that they were treated as essentially empirical parameters. The value of ν_{sp1} corresponds to a specific gravity of 0.440 g cm⁻³ and can be compared with the values of about 1.8 to 1.7 g cm⁻³ determined by gas pycnometry with helium for these foams.³ This large difference may be possibly related to some inaccessibility of the aromatic vapors to fractions of the polymeric matrix. However, there is no other indication to support this proposal. Another question that could influence this result is the value of the specific volume of the organic compounds (ν_{sp2}) used in the calculation of the volume fraction Φ_1 (eq 7). In the calculations, the liquid specific volume was used (Table 3), assuming a liquidlike mixture between the organic compounds studied and the polymeric matrix. This is questionable and could lead to values of ν_{sp1} with no physical significance. The value of δ_1 is lower than literature values for other polymers,³⁴ although determined with nonfoamed polymers and from liquid solvent/polymer solutions that are very different conditions from the vapor/polymer equilibrium. However, this low value could also be a consequence of the weak interactions between the molecules of the polymer since this is essentially a hydrophobic polyether polyurethane foam in which the forces between polymer chains are mainly of the dispersive van der Waals type. The value of r determined in this work is close to that determined in similar materials³⁵ but is different from what is usually considered a coordination number in polymer/solvent systems.³⁶ A small value of r found in this type of systems could be an indication that the sorption spaces between the polymer molecules are small.

From the initial slope of the plots of f/f^∞ vs x_2 (see Figure 8a for an example), the value of Henry's constant can be estimated, for the equilibrium of each vapor in the polyurethane, at an average temperature of 30 °C. Henry's constant is directly related to the activity coefficient at infinite dilution, γ_2^∞ , which can also be calculated from eqs 4 and 5 using the estimated parameters of Tables 2 and 3, respectively, and the definition

$$\gamma_2^\infty = \lim_{x_2 \rightarrow 0} \gamma_2$$

The values of $\ln \gamma_2^\infty$ determined in these three ways are presented in Table 5, with the differences to the value calculated from Henry's constant. The results support the analysis made above, since the values obtained by the three methods have a better agreement in the case of the aromatic vapors, and for the cyclohexane the Flory–Huggins value that is close to the Margules value, although both are slightly higher than the Henry value. The $\ln \gamma_2^\infty$ value of MEK is poorly predicted by the Flory–Huggins method, and the value is an indication that even at low pressures the amounts are over predicted. The Margules equation, however, presents itself as a good alternative in this case. The values presented in Table 5 confirm the validity of the Flory–Huggins estimated parameters for the nonpolar molecules, at low pressures. This is a region of practical interest

TABLE 5: Activity Coefficients at Infinite Dilution of Different Vapors on the Selected Polyurethane Foam (See Text), Calculated From Three Different Methods at 30 °C

vapor	method	$10^3 \ln \gamma_2^\infty$	difference (%) ^a
benzene	Henry	1.56	
	Margules	1.57	0.9
	Flory–Huggins	1.62	3.9
toluene	Henry	1.62	
	Margules	1.64	1.2
	Flory–Huggins	1.63	0.9
ethylbenzene	Henry	1.71	
	Margules	1.78	3.9
	Flory–Huggins	1.79	4.9
cyclohexane	Henry	0.87	
	Margules	0.92	5.6
	Flory–Huggins	0.94	8.1
MEK	Henry	1.96	
	Margules	2.02	3.0
	Flory–Huggins	1.74	−11.3

^a In relation to the value obtained from the respective Henry's constant.

since these foams are to be used as adsorbent supports in the purification of air streams, where usually organic vapors are found only in small amounts.

The application of a different method for the prediction of sorption isotherms was also attempted, using an equation proposed by Dubinin and Astakhov that is widely employed in the analysis of adsorption isotherms in microporous solids, at different temperatures.^{37–39} Although this equation fit quite well to the isotherms, for a given vapor, the parameters presented strong temperature dependence, which in a certain sense contradicts the fundamentals of the equation and limits its application for the prediction of isotherms at different temperatures. The fact that the data in the present work failed to be described by the Dubinin–Astakhov equation is most probably an indication that the physical process of vapor sorption in the polyurethane is rather different from the physical adsorption of gases on solid surfaces. In fact, the studied polyurethane foam has a surface area of less than 2 m² g^{−1} determined by low-temperature nitrogen adsorption.³ The hypothesis that the amounts of the studied organic compounds were adsorbed only at the surface of the foam would lead to the absurdity of having surface concentrations higher than those found for instance in microporous activated carbons.⁴⁰ This means that the organic vapors have access to a large volume, between the polymeric chains, where the nitrogen molecule cannot enter. The phenomena could be regarded as a solution of organic vapor in a solid polymeric matrix, and this is probably the reason the methods developed for solution chemistry used above lead to good results. The difference between the sorption behavior of the organic vapors and nitrogen could be related to the temperature difference at which the experimental isotherms were determined, since in the nitrogen isotherms the very low temperature (−196 °C) could most certainly difficult the capacity of the polymeric chains to accommodate sorbed molecules between them.

Conclusions

The sorption of toluene in two series of polyurethane foams with different compositions presented some differences among the foams of each series, which could be correlated with the water content used in their synthesis. The foams synthesized with less water presented a slightly high sorption capacity of toluene, and this fact was related with their high hydrophobic nature. The results suggest that these small differences could

be related to the content of polar groups in the polymeric matrix. The foams synthesized with lower amounts of water presented higher sorption amounts of toluene than those synthesized with more water, since they have a low content of urea groups in the matrix. However, the small magnitude of these effects is an indication that the interaction of the toluene vapor with the polyurethane is mainly controlled by dispersion forces.

The sorption of different vapors, at three temperatures, in one polyurethane foam presented significant differences. The differences among the isotherms expressed as n^s vs p of each vapor are essentially a consequence of the different saturation pressures at each temperature, and the activity coefficient was found to be almost independent of the temperature. This is the reason, assuming an average temperature of 30 °C, the application of the three-suffix Margules equation to the data gives a good description of the isotherms at 25, 30, and 35 °C and presents a simple method for the prediction of isotherms of each vapor in this temperature range.

The generalization of the prediction of the sorption isotherms was attempted with the fitting of the Flory–Huggins equation to the data of the isotherms of benzene, toluene, and ethylbenzene, at three different temperatures, in one data set. The parameters estimated in this way described the isotherms of these aromatic compounds with a deviation from the experimental values similar to those found on the application of the three-suffix Margules equation. With these parameters, the prediction of the isotherms of cyclohexane and MEK was attempted. In the first case, the predicted isotherm presented deviations from the experimental data comparable to those found with the three-suffix Margules equation. It should be emphasized that these predictions were made from the data obtained from the adsorption of the aromatic compounds, which is a good indication on the validity of the method used. In the case of MEK, the prediction was poor and presented an overestimation of the sorbed amounts, probably a consequence of the strong dipole moment of the MEK molecule. The parameters estimated from the sorption isotherms of the aromatic compounds could not predict the sorption isotherms of MEK, and this is most certainly due to the differences in the nature of the vapor/polymer interactions that are presented in the two cases, since the aromatic compounds are nonpolar and the MEK is a strong polar compound.

The two methods used for the estimation of sorption isotherms presented similar results when applied to vapors of nonpolar molecules. The method based in the three-suffix Margules equation could be applied to the prediction of the isotherms of MEK, but contrary to the method based in the Flory–Huggins equation, it cannot be extended to predict sorption isotherms of other vapors than those for which the parameters were determined. The reliability of the prediction at low pressures was confirmed by comparison of the activity coefficient at infinite dilution with the one determined by the Henry's law. This gives an indication that these two methods could be applied, with some restrictions, to the prediction of sorption isotherms in polyurethane at room temperatures, particularly at low pressures, which are the conditions usually found in the air filtering systems. This is important when these foams are considered for support of adsorbent materials, especially when the sorption isotherms of the resulting composite materials need to be studied.

Acknowledgment. M. L. Pinto thanks Fundação para a Ciência e Tecnologia (FCT) for a PhD grant. This work was partially made under the pluriannual funding of FCT to CQB.

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