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An improvement of the Mc Bain's microbalance to study transport of solvent vapours into polymeric films

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SUMMARY

The sorption characteristics of benzene and cyclohexane vapours in the poly(urethane-urea) (PUU) with well defined structure were measured using an improved version of the Mc Bain's microbalance. The diffusion coefficients were calculated for the different vapour activities from the kinetics of solvent uptake, i.e. the sorption isotherms over time. Sorption and diffusion coefficients measured, showed a strong dependence of the applied vapour activity. The obtained transport parameters were discussed with regard to the polymer structure. Based on the sorption and diffusion data, the pervaporation performance of the PUU-based membrane in separation of the benzene/cyclohexane mixtures was predicted and compared with the experimental pervaporation characteristic.

INTRODUCTION

Transport of vapours through polymeric films intensively studied during the past decades has again gained interest recently. This is mainly due to the fact that the increasing number of new commercial and engineering applications of polymeric materials is based on this phenomenon. Here may be mentioned the applications of polymers as protective barriers in chemical or food industries, or in membrane separation processes in recovery or recycling of organic vapours from air streams, and in the separation of aqueous-organic or organic-organic mixtures by pervaporation. Therefore, more fundamental understanding of the transport mechanism is required in order to succeed in the applications of polymers in these areas.

In dense polymer films, for which the solution-diffusion mechanism is applicable, the transport of small molecules can be investigated using permeation or sorption methods. The first ones, monitoring the permeate, are useful for systems with relatively high diffusion coefficient and rather small solubility. On the other hand, some disadvantages connected with permeation experiments, especially leakage problems or pressure affected distortions of the membranes, can be avoided in sorption methods. The gravimetric method seems to be the most common and accurate within this group of measurements. Most commercial apparatus are of beam or spring types. Another type is suspension balance where the sample is freely suspended without connection to the measuring system. For special tasks, oscillation balances like crystal balances are available.

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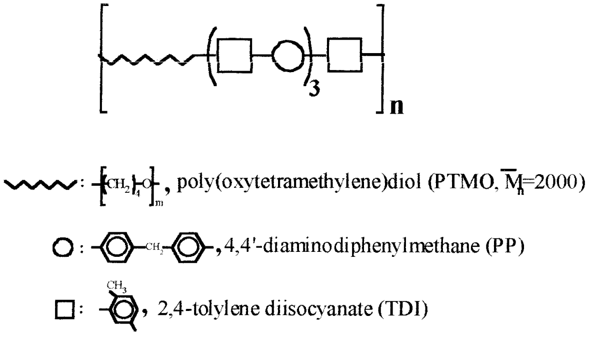
With respect to simplicity of design, quartz spring balances are particularly favourable. The classical Mc Bain's balance (1) consists of a quartz spring in a glass tube. Deflection is observed using a cathetometer.

In this work an improved version of the Mc Bain's microbalance was used to study the sorption behaviour of organic solvents in new segmented polyurethanes and poly(urethane-urea)s. These polymers were designed and synthesised with the aim of applying them as new hydrophobic membrane materials for liquid mixture separations (2,3). The Mc Bain's microbalance used in these studies enable reliable data on sorption and diffusion coefficients to be obtained in a simple way. Based on these data the behaviour of a particular polyurethane material in the presence of various solvents can be analysed and its pervaporation performance can be much easier predicted. Moreover, the sorption and diffusion data can also serve as a starting point in tailoring a polymer's structure to a given separation task.

EXPERIMENTAL

Membrane

For this study a poly(urethane-urea) (PUU) composed of soft segments based on poly(oxytetramethylene)diol of M_n=2000 and hard segments being products of the reaction of 2,4-tolylene diisocyanate with 4,4'-diaminodiphenylmethane was used. A schematic representation of a polymer structure is given in Scheme 1. The PUU was synthesised using a two step polyaddition method in DMF solution in order to obtain a polymer with a low polydispersity of hard segments along a polymer chain. The details of the synthesis and the physicochemical characteristics of this polymer along with its transport properties in the pervaporation of benzene/cyclohexane mixtures are given elsewhere (2).



Scheme I. Schematic representation of the PUU structure

Table 1. Composition and some properties of the PUU

Composition of the reaction mixture [mole]		M_n	M_w/M_n	Hard segments content (calculated) [%]	γ [g/cm^3]	T_g [°C] 20°/min
TDI : PTMO : PP	4 : 1 : 3	36500	1.6	40	1.098	-77
PTMO diol		2000	-	-	0.961	-85

Films of thickness of about 350 μm were prepared by casting a 15% solution of the polymer in DMF onto a glass plate and by evaporating the solvent at 60°C for 72 hours.

Solvents

As model solvents benzene and cyclohexane were selected since the separation of the mixtures of aromatic and aliphatic hydrocarbons by means of a pervaporation method is a main goal of our work.

Apparatus

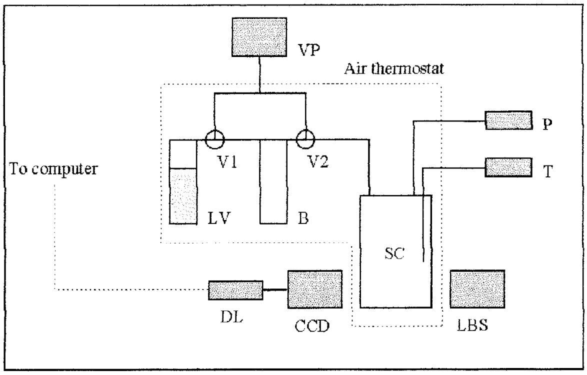


Figure1. Block diagram of the apparatus

An apparatus shown in Fig. 1 consists of the following main parts: a liquid (LV) and buffer (BV) vessels, the both made of glass, a sorption chamber (SC) made of stainless steel and an electro-optical system (LBS+CCD). The glass and steel parts are placed inside an air thermostat. The vessels and the chamber are filled with vapours or evacuated by a vacuum pump (VP) through the three-way valves (V1) and (V2). Temperature inside the chamber is monitored with a digital thermometer (T) and is maintained within ± 0.1°C. The pressure in the sorption chamber is monitored by a manometer (P) with the accuracy within ± 0.1 kP.

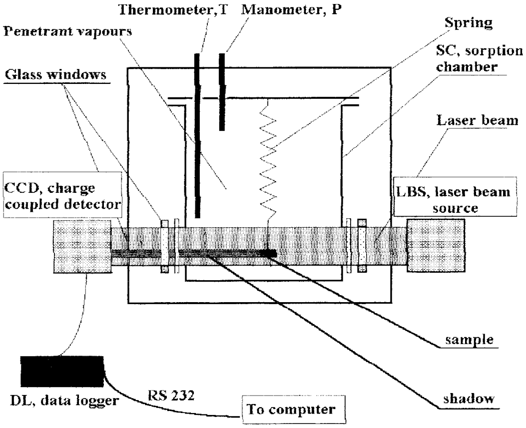


Figure 2. Vapour sorption chamber

Figure 2 shows a cross section of the sorption chamber. A sample and an indicating horizontal rod are placed at the end of a suspended metallic spring. At a bottom of the chamber there are two pairs of glass windows for lightening the rod by the laser beam source (LBS) and for recording its movement by the electro-optical system. The electro-optical recording system consists of a charge coupled detector (CCD) and a data-logging device (DL). The height of the laser beam and the length of the CCD are equal to 30 mm. When the sample weight changes with time the shadow of the rod moves along the CCD and after conditioning a signal proportional to the spring length changes are produced at the output of the detecting system. The data are collected by the fully programmable data-logger and can be transmitted to a computer by the RS 232. The data-logger has eight separately programmed channels. The programmed parameters for each channel are: sampling rate, number of points, number of points per averaging and scaling ranges. The maximal sampling rate is one sampling every 20 ms. With several channels it is possible to collect data with different sampling rate for each of the selected time intervals. It allows to adjust the number of the data points to the particular time interval according to the sorption kinetics. It is particularly important in prolonged sorption experiments due to memory limits of the data logger. It is also possible to perform the sorption experiments even in a noisy environment because of the averaging procedure applied in the system, which only requires to choose a number of samples for an average. The noises are eliminated in case the averaging period is a multiple of the spring oscillation period.

RESULTS

Typical sorption and desorption runs for various vapour activities, obtained from the microbalance output, are presented in Fig.3. as plots of the spring elongation versus time. These data were recorded for the sampling rate equal to 1s^{-1} and with the averaging equal to 10 samples per average.

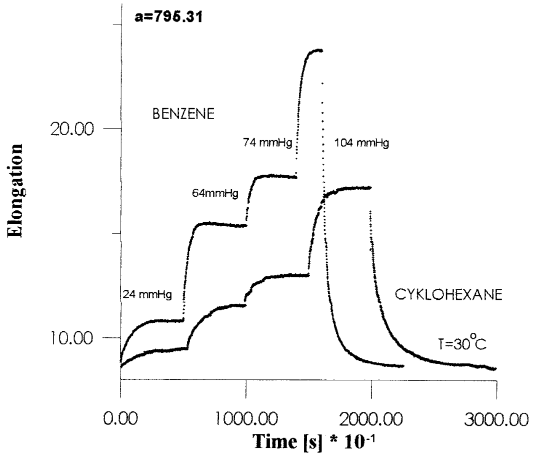


Figure 3. Experimental sorption and desorption kinetics recorded from a microbalance output.

The lack of the shock elongation at the beginning of any of the measurement series due to the pressure changes indicates the averaging period was chosen correctly.

Sorption behaviour

An example of the obtained results converted into typical mass uptake over time curves using the spring correlation parameter (a) is presented in Fig.4. The sorption isotherms of PUU at 30°C calculated from the experimental data are shown in Fig.5. The progressive increase of the solubility with increasing vapour activity can be seen for the both solvents indicating that the solubility coefficients are concentration dependent. Such distinct deviation from Henry's law suggests an important interaction between a solute and a polymer.

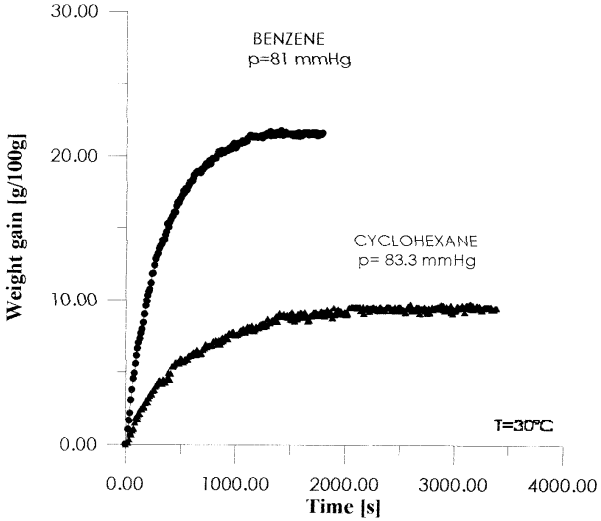


Figure 4. Typical sorption kinetics curves for the sorption of benzene at p=81.0 mmHg and cyclohexane at p=83.3 mmHg in PUU at 30°C

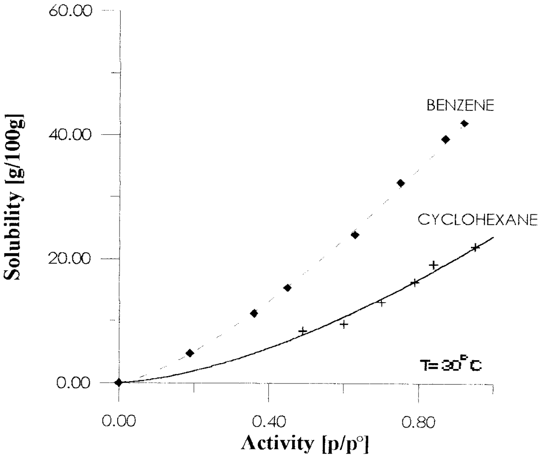


Figure 5. Benzene and cyclohexane sorption isotherms in PUU.

As can be seen from Fig. 5 this interaction is more pronounced for benzene than for cyclohexane. The ratio of the benzene to cyclohexane solubilities is in the range of 2.4 to 2.0 exhibiting a slight tendency to decrease with the increase of the vapour activity.

Diffusion behaviour

The mass transport process through a polymer film in the case of Fick's diffusion can be described using the following equation given by Crank (4):

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \cdot \sum_{n=1}^{\infty} \frac{1}{(2n+1)^2} \cdot \exp\left\{ -\frac{D(2n+1)^2 \pi^2 t}{d^2} \right\}$$

where M_t and M_∞ represent the amount of the sorbed mass at a given time t and at equilibrium respectively, d is the thickness of the film and D is the diffusion coefficient. If the relative changes in the mass sorbed are plotted as a function of the thickness-reduced square root of time and if it is assumed that diffusion is controlled by Fick's law, the diffusion coefficient can be calculated from the slope G of the linear part of this function using the following expression:

$$D = \frac{\pi}{16} G^2$$

A linear relationship up to 0.8 for the both solvents, as it is demonstrated in Fig.6, confirms the assumption that diffusion in the investigated PUU follows Fick's law.

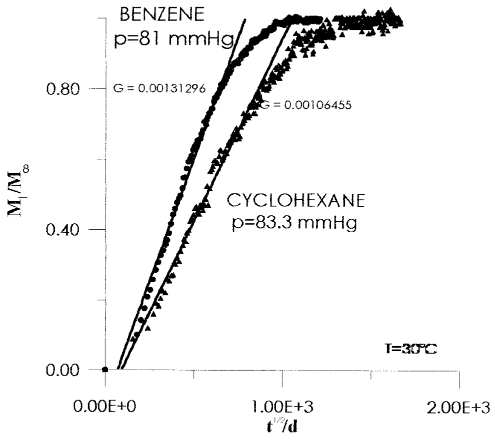


Figure 6. M_t / M_∞ versus $t^{1/2}/d$ sorption curves for the sorption of benzene (p=81.0 mmHg) and cyclohexane (p=83.3 mmHg) in PUU at 30°C.

An examination of the values of the diffusion coefficients obtained for different solvent activities reveals a significant increase in the diffusion coefficient value with the vapour activity.

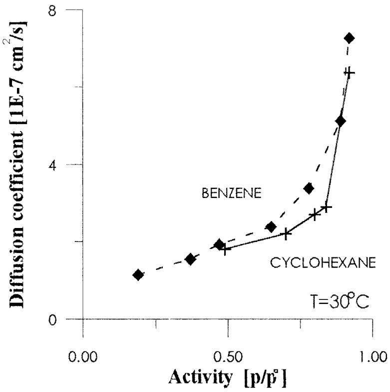


Figure 7. Diffusion coefficients D versus activity of benzene and cyclohexane in PUU at 30°C.

The experimental data presented in Fig. 7 fit an exponential relationship found for a number of other polymer-penetrant systems. The empirical relation D=$D_{c=0}$ exp(ac) was found to describe the dependence of D on penetrant concentration c (p/p_0 in this work) in the Fickian diffusion of small organic molecules in polymers above their glass transition. The explanations of this phenomenon given in literature are based on the free volume theory (5). The constant parameter a from this relationship is a property of the given polymer-penetrant system and can be interpreted as the ability of the penetrant to plasticize the polymer; i.e. to increase the polymer's segment mobility and in turn the free volume available for penetrant diffusion. The greater plasticization ability of benzene when compare with cyclohexane seems also to be responsible for its higher diffusion coefficient values since the difference in the effective sizes of the both solvent molecules is rather small.

DISCUSSION

The PUU studied in this work belongs to a group of segmented polyurethanes composed of alternating highly polar and rigid ”hard segments” and relatively long and flexible ”soft segments”. These polymers exhibit microphase-separated morphology due to thermodynamic incompatibility of the hard and soft blocks. It has been shown (6) that the degree of phase separation and the domain structure result from the chemical nature of both segments, their composition and molecular weights. Although the hard domains are unpermeable to gases and liquids, they affect the overall transport by reducing the area available for transport, by increasing tortuosity of the permeation path, and by supressing membrane swelling. However, the major factors responsible for transport behaviour of the PUU films seem to be the structure and mobility of the segments creating soft domains.

The PUU used in this work can be regarded as almost completely phase separated system due to the T_g value of its soft segments which is very similar to the T_g value of the net PTMO diol (Table I). This means that transport of small molecules occurs in the ruberry regions entirely formed by the PTMO-based soft segments, whereas the hard segments segregated into hard domains act as physical crosslinks in the soft-segment matrix.

The solution-diffusion mechanism is generally accepted to describe the transport of molecules in dense membranes. According to this model, the permeation process can be devided into three steps: sorption into the membrane, diffusion through the membrane and desorption at the opposite side of the membrane. The membrane selectivity comes from the different solubilities and diffusivities of the components in the membrane. Although multi-component permeation differs from single-component permeation due to the plasticization and coupling effects, the sorption and diffusion coefficients can serve to obtain the first overview of transport properties of the PUU membrane when applied in the separation of benzene/cyclohexane mixtures.

As can be seen from the data presented in Fig.5 and 7, the both sorption and diffusion steps promoting benzene over cyclohexane cause the PUU membrane is benzene permselective. On the other hand, neither the solubility selectivity, $\alpha_s=2.4\div2.0$, nor the diffusivity selectivity, $\alpha_D<2$, defined as the ratio of the benzene and cyclohexane solubilities or diffusivities, suggests the PUU membrane can exhibit separation ability interesting from the commercial point of view. Despite the rather high permeability rate expected for this membrane, the selectivity is not thought to reach the maximum value of 4.8 being a product of the both selectivities. The separation results obtained for the pervaporation of the benzene/cyclohexane mixture containing 5% by weight benzene, at 30 °C under minimum permeate pressure (below 1 mm Hg) compare well with the prediction made from the sorption data. The permeability rate estimated for this process, F=42 kgμm/m^{2}h, was high and the pervaporation selectivity, $\alpha=3.3$, was below the calculated value as expected. Moreover, the strong concentration dependencies of the both sorption and diffusion coefficients suggest the successive decrease of the membrane selectivity with the increase of the benzene content in the separated mixture. Therefore, some modifications of the PUU structure have to be performed in order to obtain the membrane material with better transport properties. The one possible way to improve selectivity of the membrane is to increase solubility selectivity of the PUU. It can be achieved by synthesising the PUU the soft segments of which exhibit lower affinity towards cyclohexane. On the other hand, the application of the PUUs with a high hard segments content should suppress membrane swelling and prevent the deterioration of its selectivity when used in the separation of the benzene rich mixtures. As has been found out recently, the membrane selectivity can also be improved using PUUs with PTMO-based soft segments of a low molecular weight. The influence of the soft and hard segment structure and length on the sorption and diffusion of organic solvents in the segmented polyurethanes will be a subject of a separate paper.

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