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Behaviour of water/ethanol mixtures in the interfacial region of different polysiloxane membranes—a molecular dynamics simulation study

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Results from molecular dynamics (MD) simulations in the interfacial region of three polysiloxanes, polydimethylsiloxane (PDMS), polyoctylmethylsiloxane (POMS) and polymethylphenylsiloxane (PMPhS), and ethanol/water mixtures are reported. The behaviour of all polysiloxanes in contact with the same solvent composition is very similar. The ethanol molecules accumulate at the surface of the polysiloxanes and the polymers begin to swell. The diffusive movement of these partly sorbed ethanol molecules is strongly hindered in the direction of the water phase. Parallel to the polymer surface the diffusion of the ethanol is faster but still slower than in the free diffusion case. The ethanol molecules in the interfacial layer show a favourite orientation wherein the hydrophobic parts point in the direction of the polymer and the hydrophilic parts point in the direction of the water molecules. The ethanol concentration of the feed has a strong influence on the interfacial behaviour. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Molecular dynamics (MD) simulations have proved to be useful for studying the transport of small penetrant molecules through amorphous polymer membranes[1]. They have been already used to investigate the diffusion of small gas molecules (H_2, N_2, O_2, CH_4) in common polymers like polyethylene (PE)[2-4], polypropylene (PP)[5], polyisobutylene (PIB)[4,6] and polydimethylsiloxane (PDMS)[2-8]. However, diffusion alone does not describe the transport process across a membrane sufficiently because the solubility of the permeant molecules in the membrane is a determining factor as well. In case of the pervaporation where a membrane separates a mixture of liquids, the solubility is usually even more important for the selectivity of the separation process[9]. To investigate this factor in detail it should be interesting to carry out MD simulations at the interface between the polymer and feed.

In a previous paper[10] results of MD simulations in the bulk and in the interfacial region of PDMS and a water/ethanol feed were reported. It could be shown that in the bulk region with inserted water and ethanol molecules the movement of the penetrants has the character of a jump diffusion, where the ethanol molecules stay longer in the occupied cavities than the water molecules. Thus the calculated diffusion coefficients, which agree well with the experimental values, are greater for the water than for the ethanol molecules, a fact that can be related to simple size effects.

Despite this finding, PDMS is preferentially permeable to ethanol because of the essentially higher solubility of ethanol as compared with water[11]. The simulations in the interfacial region reflected this preferential solubility. During the chosen simulation time of 1 ns, the ethanol molecules accumulated at the hydrophobic PDMS surface and showed a favourite orientation wherein the hydrophobic parts of the ethanol molecules pointed in the direction of the polymer and the hydrophilic parts pointed in the direction of the water molecules. This qualitative behaviour—which is completely in line with experimental findings for PDMS in contact with water/ethanol mixtures (e.g. hydrophobicity of the polymer, a certain level of amphiphilic behaviour for the ethanol molecule and the observed pervaporation properties)—demonstrates the ability of currently available molecular modelling techniques and advanced force fields to describe complex interface systems correctly.

In this paper we wish to extend our MD simulations to the interfacial region of two other polysiloxanes, polyoctylmethylsiloxane (POMS) and polymethylphenylsiloxane (PMPhS), in contact with a feed mixture of 10 wt% ethanol and 90 wt% water. In addition, we wish to complement the evaluation for the MD simulation of PDMS in the interfacial region. Furthermore, as compared with[10], additional parameters for the quantitative characterization of the interface behaviour will be determined and utilized to compare the results for the different polysiloxanes.

MODEL AND SIMULATION DETAILS

The structures of the polysiloxanes investigated are shown in *Table 1*. In order to minimize end-group effects, the simulations were carried out with a single polymer chain in the simulation box. Consequently, for about the same box size, the degree of polymerization, *P*, is different for each polymer (see *Table 1*). No crosslinks and branches have been inserted.

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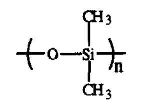
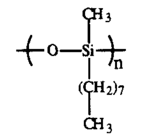
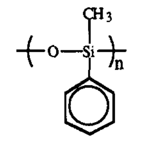
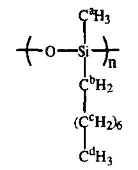
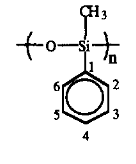
Table 1 Structure, density (d) and degree of polymerization (P) of the polysiloxanes

Polymer	Structure	$M_{(\text{Repeat unit})}$ (g/mol)	$d_{(\text{Polymer}, T = 300\ K)}$ (g/cm^3)	P
PDMS		74.2	0.95[17]	220
POMS		172.3	0.91[17]	90
PMPhS		136.2	1.11[17]	133

[a]Data from [12]

Table 2 Partial charges of the atoms for POMS and PMPhS

Polymer	Structure	Atom type	Partial charges
POMS		Si	0.640
		O	-0.440
		$C(CH_3)^a$	-0.259
		$C(CH_2)^b$	-0.206
		$C(CH_2)^c$	-0.106
		$C(CH_3)^d$	-0.159
		H	0.053
PMPhS		Si	0.690
		O	-0.440
		$C(CH_3)$	-0.259
		C(ph.)^1	-0.150
		C(ph.)$^{2\text{-}6}$	-0.127
		$H(CH_3)$	0.053
		H(ph.)	0.127

The InsightII/Discover software of Molecular Simulations was used for the construction and the atomic simulations. For the potential energy calculation the pcff[13] force field was applied. The details of calculation of the Coulombic interactions as well as the partial charges and the force field parameters for PDMS, ethanol and water molecules have already been given in[10]. The partial charges for POMS and PMPhS are listed in *Table 2**.

All calculations were performed on two IBM RS6000 workstations (models 340 and 3BT) and on the CRAY C916 of the Deutsches Klimarechenzentrum (DKRZ) in Hamburg.

Before each interface box was assembled, a pure polymer box and a pure feed box were packed and equilibrated separately (the exact packing and equilibration procedure is described elsewhere[14]). During these procedures, the periodic boundary conditions are effective only in two dimensions. In the third dimension penalty surface potentials force the non-periodic coordinates of the constituent atoms into a layer of a given thickness which results from the other two box lengths and the density of the system. After the complete refinement of each individual box, the polymer and the feed boxes were layered onto each other. The number of molecules included and the box lengths of the layered boxes for the different polysiloxane feed systems are listed in *Table 3*.

The MD production runs were performed at 300 K with NVT (constant number of atoms–constant volume–constant temperature) ensembles under three-dimensional periodic boundary conditions (i.e. there were always two interfaces existing along the c-axis of a model). The cut-off distance for all non-bond interactions was chosen to be 12.0 Å. For the dielectric constant a value of $\epsilon = 1.0$ was taken which is necessary for the full consideration of hydrogen bonds in the pcff force field. Newton's equations of motion were solved with a time step of 1 fs. Snapshots of the positions and velocities of all atoms were taken every 500 fs and saved in a history file. The length of the simulation for all polysiloxane/feed systems was 1 ns. In the case of PDMS after 1 ns where all but one of the original ethanol molecules were already sorped at the polymer surface, a suitable part of the water molecules was replaced statistically by new ethanol molecules to come closer to the experimental reality where a steady flux of fresh solvent mixture is always retained. Afterwards, the MD run was restarted for an additional 800 ps (cf. [10] and *Figure 10*).

RESULTS AND DISCUSSION

The general interfacial behaviour of POMS and PMPhS against a feed mixture of 10 wt% ethanol and 90 wt% water is very similar to that already observed for PDMS under the same simulation conditions[10]. After a short simulation time the ethanol molecules of the feed mixture begin to accumulate at the hydrophobic polymer surface. During this enrichment of the ethanol molecules the polysiloxane surfaces begin to swell.

Figure 1 shows normalized density profiles of the POMS/feed system after a simulation time of 1 ns. Inside the feed the ethanol and water molecules are segregated completely and, thus, a new interface between the two feed components

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*The other force field parameters required for these two polymers are available from the authors upon request

Table 3 System classifications

Polymer	Feed	Number of polymer molecules	Number of water molecules	Number of ethanol molecules	Box length, $a = b$ (Å)	Box length, c (Å)
PDMS	10 wt% ethanol 90 wt% water	1	460 (414)[a]	20 (38)[a]	24.5	73.3
PDMS	100 wt% ethanol	1	/	160	24.5	73.2
POMS	10 wt% ethanol 90 wt% water	1	460	20	24.5	73.1
PMPhS	10 wt% ethanol 90 wt% water	1	460	20	24.5	71.1

[a] New feed after a simulation time of 1 ns

is developed. This behaviour of POMS is very similar to that observed for PDMS[10]. In the case of PMPhS (*Figure 2*) two ethanol molecules (one at each surface) are already penetrating into the polymer after the same simulation time of 1 ns. Whether this is really due to differences in the polymer or more a statistical effect cannot be answered here. This decision would need additional simulations. However, the overall width of the swelling layer actually does seem to be greater in the case of PMPhS than for PDMS and POMS at the same simulation time.

For all polysiloxane/feed systems detailed investigation of the movement of ethanol molecules shows that an ethanol molecule, once it has reached the polymer surface, moves mostly in the plane of the interface (*ab*-plane) and only little in the direction of the feed (*c*-axis). This behaviour can be recognized clearly in a plot of the mean squared displacement, *MSD*(t), of the molecules averaged over all possible time origins along the different axes against the simulation time, t. *Figure 3* shows $MSD_{a/b/c}(t)$ *versus* t for the ethanol molecules at the POMS surface during the simulation time of 900–1000 ps. While the *MSD*(t) components of the accumulated ethanol molecules along the *a*- and *b*-axes are comparable within the expected error range, the mobility of these molecules along the *c*-axis is obviously smaller. The determined slopes of $MSD_{a/b}(t)$ are four times greater than the slope of $MSD_c(t)$. The corresponding values for the other two polysiloxanes are very similar. However, distinctly higher diffusion coefficients were found for the ethanol molecules in a simulation of a pure ethanol/water (10 wt%/ 90 wt%) mixture without contact with a polymer by utilizing the same simulation parameters under three-dimensional periodic boundary conditions. As expected, here the mean squared displacements are identical in all three directions. The slopes are double those for the ethanol layer in the *a*- and *b*-directions of the respective polymer/ feed models. Thus, the diffusion in any direction inside the pure feed is considerably greater than in the two directions inside the plane at the polymer interface. Consequently, the movement of ethanol molecules in the layer formed at the hydrophobic polysiloxane surface seems not only to be hindered in the direction of the interface (– *c*) but also in the directions parallel to the surface. This behaviour is caused by specific polymer–ethanol interactions.

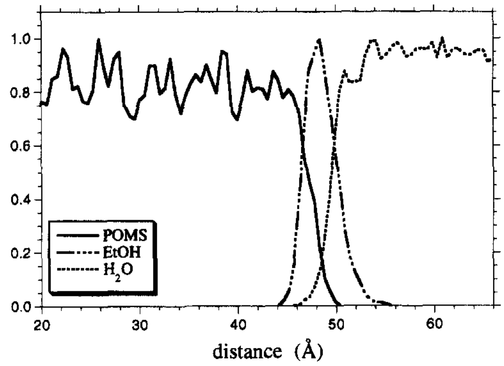

Figure 1 Normalized density profiles of POMS and a water/ethanol (90 wt%/10 wt%) feed after a simulation time of 1 ns (the profiles were an average over 41 snapshots from 980 to 1000 ps)

However, a different behaviour can be observed in the simulation of PDMS against a pure ethanol feed. In this case, the additional polarizing effect of the interactions between the hydrophilic ends (OH) of the ethanol molecules and the water molecules is removed. Here, for comparability

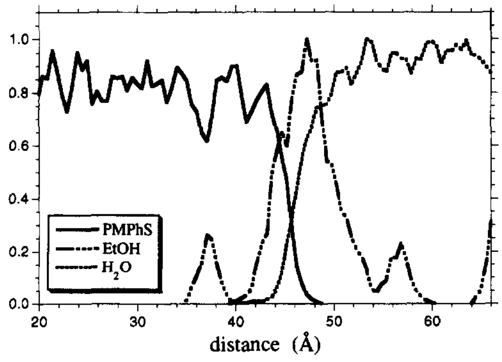

Figure 2 Normalized density profiles of PMPhS and a water/ethanol (90 wt%/10 wt%) feed after a simulation time of 1 ns (the profiles were an average over 41 snapshots from 980 to 1000 ps)

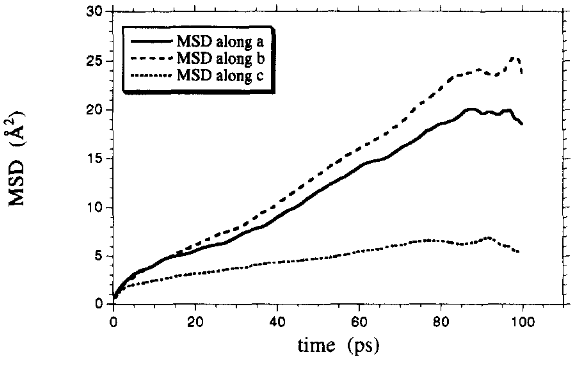

Figure 3 Mean squared displacement (*MSD*) along the different axes of the ethanol molecules in the layer formed at the POMS surface, obtained from the simulation time period of 900–1000 ps

reasons, the $MSD(t)$ curves were calculated just for ethanol molecules which were closer than 6 Å to the polymer surface. Then, in comparison with the complete polymer/ethanol/water model, the main result is a considerable increase (by a factor of about 4) of the diffusivity (slope of the $MSD_c(t)$ *versus t* plot) of the ethanol molecules towards the *c*-axis of the model. The diffusivities along the polymer surface (*a*- and *b*-axes), on the other hand, are about the same as observed from the $MSD_{a/b}(t)$ slopes of the ethanol molecules in the polymer/ethanol/water models. These observations basically mean that, in the polymer/ethanol case, desorption of ethanol molecules which were already adsorbed at the polymer surface is less restricted than in the polymer/ethanol/water case. This underlines the general experimental observation that the relevant material properties of pervaporation membranes (e.g. swelling of the polymer, solubility and diffusivity of small molecules in the polymer matrix) are very sensitive to the composition of the feed mixture to be separated.

In order to determine the polymer–solvent interactions in more detail, the orientation of the ethanol molecules in the forming layer at the polymer surface was also considered. For this purpose, the carbon–carbon and carbon–oxygen bonds were described by two vectors, having their origin in the more hydrophobic part and their direction towards the more hydrophilic part of the respective bond. As polymer surface an *ab*-plane was taken. The vectors were calculated for various time periods of 20 ps (41 snapshots, see Section Section 2) for all ethanol molecules at the interface. Then, the determined frequencies of the angles were weighted by the circumference of the base surface of the cone which is generated by all vectors with the same angle to the *ab*-plane. Hence the weighting factor was 1/cos(angle vector-plane). The sum of all frequencies was adjusted to 100% whereby the angles were grouped into intervals of 5°.

Figure 4 shows the angle distribution for the ethanol molecules in a pure feed mixture of 10 wt% ethanol and 90 wt% water relative to an arbitrarily chosen plane (here: *ab*-plane) inside the simulation box without any polymer contact. As expected, all angles occur with about the same frequency within the error range. The average value, which is indicated by the dashed grey line, corresponds to 100 divided by the number of the chosen angle intervals (= 36).

In contrast to this uniform distribution a completely different behaviour is observed in the case of the ethanol molecules in the forming adsorption layer at the polysiloxane surfaces. *Figures 5 and 6* display this angle distribution at the POMS and at the PMPhS surface. It is clearly seen that the distributions are monomodal whereby nearly all vectors have positive angles to the polymer surface. Thus, the more hydrophilic part of the respective bonds points towards the water phase and the more hydrophobic part of the respective bonds points towards the polymer surface. This distinct influence is confirmed by the fact that the distribution in the case of the more polar C–O bond is less broad and shifted to larger angles. The orientation distributions of both vectors are very similar for POMS and PDMS[10] but broader for PMPhS. This finding, together with the differences found between the density profiles of PMPhS (*Figure 2*) on the one hand and POMS

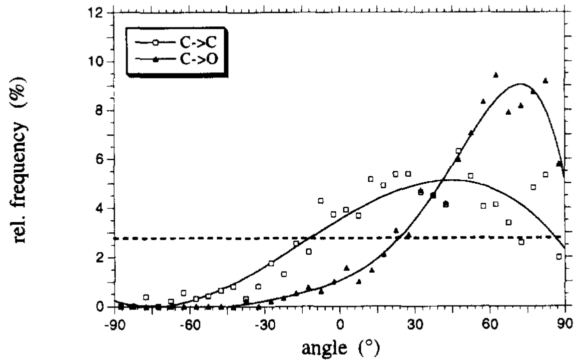

Figure 5 Weighted angle distribution of two selected vectors inside the ethanol molecules to the polymer surface for the system POMS/ethanol:-water (10 wt%:90 wt%) after a simulation time of 800 ps (see text)

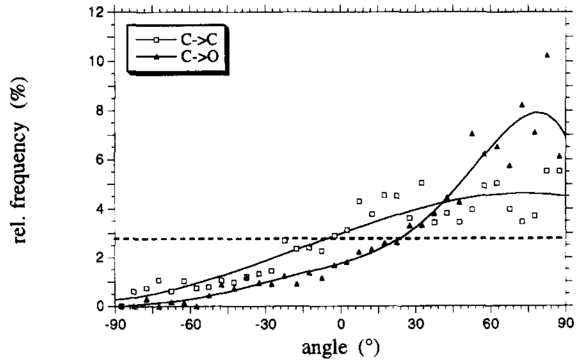

Figure 6 Weighted angle distribution of two selected vectors inside the ethanol molecules to the polymer surface for the system PMPhS/ethanol:water (10 wt%:90 wt%) after a simulation time of 800 ps (see text)

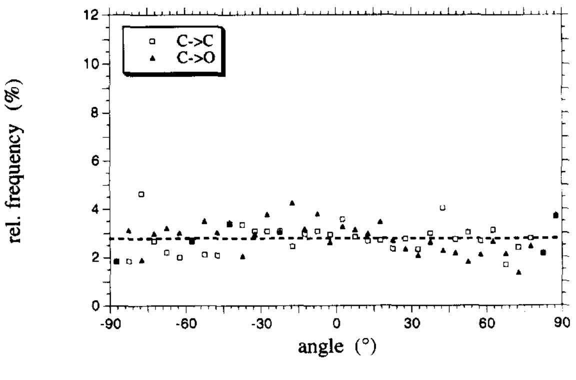

Figure 4 Weighted angle distribution of two selected vectors inside the ethanol molecules to an arbitrarily chosen plane (here: *ab*-plane) for a water/ethanol (90 wt%/10 wt%) mixture without polymer contact (see text)

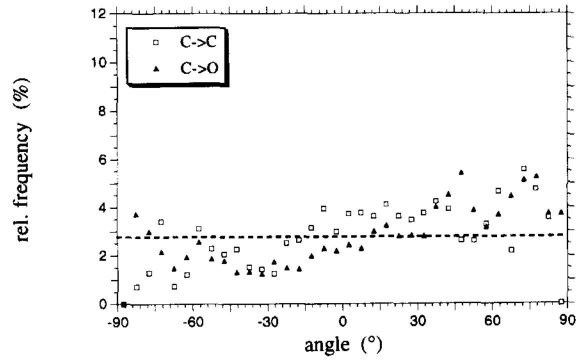

Figure 7 Weighted angle distribution of two selected vectors inside the ethanol molecules which are closer than 6 Å to the polymer surface for the system PDMS/ethanol (100 wt%) after a simulation time of 400 ps (see text)

(*Figure 1*) and PDMS ([10]) on the other, may indicate a slightly lower hydrophobicity of the PMPhS surface, although some caution is necessary owing to possible statistical problems.

Again, a considerably different behaviour is seen for the interface simulation of PDMS in contact with a feed of pure ethanol. *Figure 7* shows the orientation angle distribution of the ethanol molecules which are closer than 6 Å to the PDMS surface. Here only a slight preference of positive angles is observed. Thus, the presence of the water phase is very important for the orientation of the ethanol molecules towards the polymer surface.

This influence of the water molecules (or, more generally, the feed composition) can also be observed by means of the pair correlation functions of the silicon atoms of the polymer backbone with the oxygen and the beta carbon atoms of the ethanol molecules, respectively. In *Figures 8 and 9* these pair correlation functions for the two investigated feed compositions in contact with PDMS are shown. To compare similar degrees of swelling, the correlation was examined after different simulation times for an interval of 20 ps in each case. In detail, these were 780–800 ps for the feed mixture of 10 wt% ethanol and 90 wt% water and 380–400 ps for the pure ethanol feed. The surface silicon atoms are taken above $c \geq 40$ Å and for the pure ethanol feed all ethanol molecules were considered for $c \leq 52$ Å, while for the feed mixture all ethanol molecules at the interface were taken into account. For both feed compositions it may be clearly recognized that the separation distances are greater for Si–O than for Si–C^{β}.

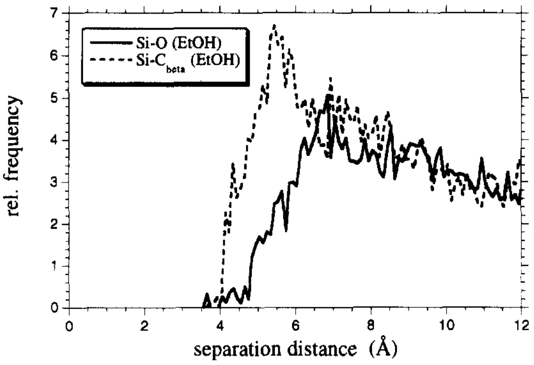

Figure 8 Pair correlation function of the silicon atoms of the polymer with the oxygen and beta carbon atoms of the ethanol molecules for the system PDMS/ethanol:water (10 wt%:90 wt%) (see text)

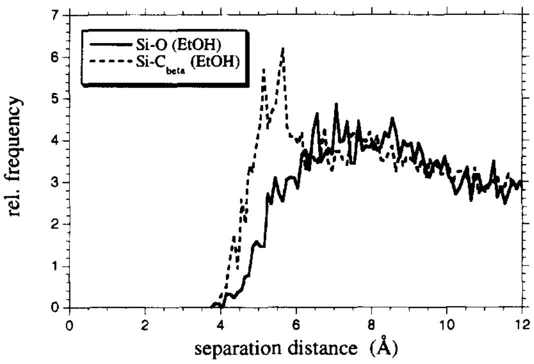

Figure 9 Pair correlation function of the silicon atoms of the polymer with the oxygen and beta carbon atoms of the ethanol molecules for the system PDMS/ethanol (100 wt%) (see text)

The obviously greater difference between these two interactions in the case of the feed mixture of 10 wt% ethanol and 90 wt% water confirms nicely the results of the angle distributions. This fact is reflected more quantitatively by the quotient of the integrals A for the same interval of separation distance (0–12 Å), which has the value $A_{(\mathrm{Si-O})}/A_{(\mathrm{Si-C}(\beta))} = 0.89$ in case of the pure ethanol feed and $A_{(\mathrm{Si-O})}/A_{(\mathrm{Si-C}(\beta))} = 0.76$ in case of the feed mixture.

Although, given the nature of the reported simulations, it would be intriguing to estimate also surface energies and tensions, the very complex nature of the interfaces observed here prevented such an attempt, at least in this investigation. To date, reports of surface energies from MD simulations in the literature are usually restricted to simpler systems. Misra *et al.*[15], for instance, investigated interfaces between amorphous polymers and vacuum, whereas Thompson *et al.*[16] considered two immiscible, simple Lennard-Jones fluids in contact with an impenetrable metal surface.

Figure 10a gives a qualitative picture of the initial sorptive behaviour of the ethanol molecules at the PDMS surface, while *Figure 10b* considers an influx of additional ethanol molecules (see Section 2).

SUMMARY

In contrast to the bulk simulations[17] of PDMS and POMS with inserted ethanol and water molecules where a distinctly slower diffusion of the permeants in POMS was observed, the simulations in the interfacial regions indicate no pronounced influence of the side-chain modification of the polysiloxanes, except that the PMPhS surface is very likely a little bit less hydrophobic than the other two. However, the simulations discussed above for the polymer/ethanol/water and polymer/ethanol models reveal that the interfacial behaviour of polymers utilized in pervaporation is very sensitive to the solvent composition, a situation also clearly found experimentally.

In the case of the polymer/ethanol/water models the two feed components separate widely during the initial stages of

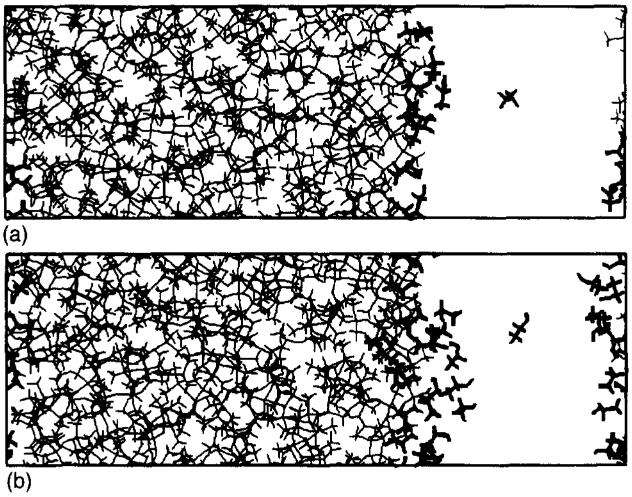

Figure 10 (a) Interface of the system PDMS/ethanol:water (10 wt%:90 wt%) with the original feed after a simulation time of 1 ns (water molecules omitted for the sake of clarity). Polymer and ethanol molecules represented by thin and bold lines, respectively. Note that, owing to periodic boundary conditions, there are actually two interfaces (left and right). (b) Interface of the same system as discussed in (a) after an additional simulation time of 0.8 ns with additional ethanol feed (see Section 2)

sorption, whereby the ethanol molecules accumulate at the hydrophobic surfaces of the polysiloxanes. This is again in line with experimental findings e.g. showing that the solubility of ethanol is approximately 760 times higher in bulk PDMS than that of water[18].

Once they have reached the polymer surface the ethanol molecules move mostly in the plane of the interface and only little in the direction away from the polymer. In comparison with free ethanol molecules in a pure feed mixture (10 wt% ethanol/90 wt% water) without polymer, the ethanol molecules near the polymer surface move more slowly. Thus, the movement of the accumulated ethanol molecules is not only hindered in the direction of the water phase but also by specific polymer–ethanol interactions at the interface.

The ethanol molecules near the polymer surface on average show a favourite orientation wherein the hydrophobic parts point in the direction of the polymer and the hydrophilic parts point in the direction of the water layer.

All the above results confirm that MD simulations are suited in principle for the investigation of important aspects of pervaporation processes. The main advantage of this approach consists in the atomic-scale resolution which, for the systems of interest here, cannot (at least currently) be obtained by any experimental technique.

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