The L/L Interface and Adsorption of SCN$^-\text{Anions as Studied by Different Molecular Simulation Techniques}$

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Different approaches are used for the modeling of the liquid/liquid interface and the adsorption of SCN$^-$ anions: (A) the self-consistent mean field approach, (B) Metropolis Monte Carlo and (C) Molecular Dynamics Simulation. The general picture of the interface agrees quite well with the three methods. Methods B and C provide in principle a more accurate picture of details and of adsorption but they are still not practical to compare a large number of systems of dilute electrolytes which the SCF method can easily do.

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Our area of interest is the potentiometric and voltammetric behavior of ion-selective electrodes of the “liquid membrane” type. The essential part of these electrodes is a gelled organic solution, the membrane, which is contacted with aqueous solutions on both side. The interpretation of electrochemical experiments at the membrane/solution liquid/liquid interface relies heavily on ideas about the molecular structure and composition of the interface. This information is difficult to get from experiments and therefore a variety of models has been used. For electrochemistry one needs to simulate many systems with different compositions, particularly with different electrolyte concentrations. In this work we present data about the structure of the interface and about adsorption of thiocyanate, a simple ion that is suitable for nonlinear spectroscopic studies of surface concentration and orientation. We compare results obtained by three different computer simulation techniques: self-consistent mean field (SCF), Metropolis Monte Carlo (MC) and Molecular Dynamics (MD). The SCF model uses a lattice, symbolic atoms and real chains, with realistic interaction parameters. In the other two models we replaced the membrane with an organic liquid, 1,2-dichloroethane. This liquid is, however, resembling the most frequently used membrane polymer, PVC. In this short paper we present more details about the MC simulation, other details will be published later.

Computational details

Simulation of the water/DCE interface

Monte Carlo and molecular dynamics simulation of the water/DCE interface has been performed on the (N,V,T) ensemble at 300 K with 536 water and 120 DCE molecules. The simulation box has had a rectangular shape; the length of its edge along the X-axis (i.e., perpendicular to the interface) has been set to 50.432 Å, whereas the other two edges have been 25.216 Å long. The water molecules have been modeled by the SPC/E potential, in which the H atoms are located at a distance of 1.0 Å from the O atoms, forming a bond angle of 109.5°. For the DCE molecules a rigid potential model, with literature data has been used. In this model the CH₂ groups are treated as united atoms, the $r_{CH_2-Cl}$ and $r_{CH_2-CH_2}$ bond lengths are set to 1.831 Å and 1.522 Å, respectively, whereas the Cl-CH₂-CH₂ bond angle is 108.8°. Since this model is rigid, it cannot account for the trans/gauche equilibrium of the molecules. Therefore, in the simulations we used 80 DCE molecules of trans and 40 ones of gauche geometry, reproducing the experimentally observed trans/gauche ratio of 2:1. The energy of the system has been calculated as the sum of the pair interaction energy of all possible atom pairs in all possible molecule pairs. The electrostatic interaction of two atoms is regarded as the Coulombic interaction of their (fixed) fractional charges, whereas the non-electrostatic part of their interaction is described by a Lennard-Jones potential. All intermolecular interactions have been truncated to zero beyond the center-center distance of 12.5 Å. The fractional charges $q$ and Lennard-Jones parameters $\sigma$ and $\epsilon$ of the models are summarized in Table 1.

<table>
<thead>
<tr>
<th>molecule</th>
<th>atom</th>
<th>$q/e$</th>
<th>$\sigma$/Å</th>
<th>$\epsilon$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>O</td>
<td>-0.8476</td>
<td>3.166</td>
<td>0.650</td>
</tr>
<tr>
<td>H</td>
<td>0.4238</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DCE</td>
<td>CH₂</td>
<td>0.227</td>
<td>3.98</td>
<td>0.4834</td>
</tr>
<tr>
<td>Cl</td>
<td>-0.227</td>
<td>3.16</td>
<td>2.120</td>
<td></td>
</tr>
<tr>
<td>SCN$^-$ ion</td>
<td>C</td>
<td>0.14</td>
<td>3.35</td>
<td>0.425</td>
</tr>
<tr>
<td>N</td>
<td>-0.58</td>
<td>3.31</td>
<td>0.310</td>
<td></td>
</tr>
</tbody>
</table>
The simulations have been performed using existing program packages. In a Monte Carlo step a randomly selected molecule has been translated randomly by a distance no more than 0.5 Å, and rotated around a randomly selected space-fixed axis by no more than 30°. At the beginning of the simulation the water and DCE phase have been equilibrated separately in cubic simulation boxes with the edge length of 25.216 Å by performing 10^6 Monte Carlo moves in each phase. Then the two boxes have been unified, and the system has been further equilibrated by performing another 10^6 moves. Finally, in the production phase 5000 sample configurations, separated by 10^6 Monte Carlo moves each, have been saved for further evaluation.

**Simulation of a SCN⁻ ion at the water/DCE interface**

In this simulation one SCN⁻ ion, modeled by generic LJ parameters for the atoms and a charge distribution obtained from quantumchemical calculations, has been added to the system described above. The co-linear r_{SC} and r_{CN} bond lengths have been 1.69 Å and 1.15 Å, respectively. The interaction parameters of the SCN⁻ ion are also included in Table 1. In order to keep the SCN⁻ ion at the interface (i.e., in the region where the water density drops from 90% to 10% of its bulk value) and to sample its position along the X axis uniformly in this region, we have used the adaptive umbrella sampling technique. This system has been equilibrated through 10^6 Monte Carlo moves. Then 500 sample configurations, separated by 10^6 moves each, have been saved for further analyses. MD results are not yet available for SCN⁻.

**SCF analysis**

The membrane material is modelled as a hydrophobic chain molecule consisting molecule segments of type A. Water molecule is modelled as dipole and potassium ions are represented with single segments, while the SCN⁻ anion as a molecule is modelled as dipole and potassium ions are molecule consisting molecule segments of type A. Water available for SCN⁻.

**Results and discussion**

**Water/DCE interface**

**Density profiles.** The molecular number density profiles of the water and DCE molecules obtained by MC are shown in the top part of Fig. 1. As is seen, both profiles change smoothly from the bulk value to zero within an about 5 Å wide interval. However, since these profiles are statistical averages, their observed smoothness can still be compatible with the presence of molecular level roughness (e.g., water fingers) in the interface. The obtained results are in agreement with previous results of Benjamin.

**Orientation of the water molecules relative to the interface.**

The orientation of a water molecule relative to the interface is characterized here by three angles, formed by the dipole vector, the normal vector, and the vector joining the two H atoms (H-H vector) of the water molecule with the vector perpendicular to the interface pointing to the aqueous phase. These angles are denoted as α, β and γ, respectively. It should be noted that these angles are not independent, and the joint statistical distribution of these angles cannot be determined from the individual distributions. It should also be noted that, contrary to the molecular dipole vector, the molecular normal and H-H vectors can be equally directed in two opposite directions, and there is no physical way to distinguish between them. Therefore, the β and γ angles can only be scattered between 0° and 90°, and thus their cosines between 0 and 1, whereas the value of α can fall in the entire angular range of 0°-180°, and hence cosα between -1 and 1. As a consequence, random orientation of the water molecules corresponds to the <cosα> value of 0, and to the <cosβ> and <cosγ> values of 0.5, where <<...>> denotes ensemble average.

In order to characterize the preferential orientation of the water molecules along the interface normal, we have calculated the <cosα>, <cosβ>-0.5) and <cosγ>-0.5) profiles across the interface. These profiles are shown in Fig. 1, multiplied by the molecular number density profile of water ρ_w. As is seen, the obtained orientational profiles start to deviate from zero (i.e., the value characteristic of bulk water) at around ±18 Å, i.e., significantly further apart from the interface than where the water density starts to decrease. Therefore, we have divided the
water-containing part of the system into three different regions. Region I is bulk-like water beyond ±18 Å. In region II, between ±15 Å and ±18 Å the density of water is still the same as in the bulk, however, the orientation of the molecules is already influenced by the vicinity of the interface. Finally, region III between about ±10 Å and ±15 Å is the interfacial region, where the density of water drops to zero, whereas that of DCE increases from zero up to its bulk value.

It is seen from Fig. 1 that the obtained cos α profile is negative between ±18 Å and ±12 Å, indicating that the dipole moment of the water molecules are pointing preferentially towards the DCE phase. This tendency is then reverted in the DCE-rich side of the interface. However, it should be noted that, since preferential perpendicular orientation cannot be distinguished from random orientation or from equally preferred inward and outward orientations solely on the basis of cos α, the obtained orientational profile should be interpreted with care. Fig. 2 shows the distribution of cos α in the three regions separately. As is seen, in the interfacial region the obtained distribution goes through a maximum around 0, indicating that here the preferential orientation of the water dipoles is parallel to the interface. Hence, the negative peak of the cos α profile between ±18 Å and ±12 Å solely shows that when deviating from their preferential parallel orientation, the water dipoles slightly prefer to point to the DCE rather than to the aqueous phase. When analyzing the cos β<0.5> and cos γ<0.5> profiles it is seen that the former has a pronounced positive, whereas the latter a negative peak in regions II and III. Since, contrary to P(cos α), the P(cos β) and P(cos γ) distributions (not shown here) are monotonous functions in all the three separate regions, the interpretation of these profiles are rather straightforward. Positive values indicate preferential parallel, whereas negative values preferential perpendicular orientation to the interface normal. Thus, the present results clearly show that in region II as well as in most parts of the interface the water molecules are preferentially oriented parallel to the interface. It is also seen that below ±12 Å, where the density of water is less than 15% of its bulk value, the orientational preference is slightly changed. Here the H-H vector is preferentially perpendicular to the interface, whereas the molecular normal vector has no orientational preference any more. This preferential orientation is similar to what has been found by Benjamin.

We have also analyzed the influence of the interface on the hydrogen bonding structure of the neighboring molecules. For this purpose, we have calculated the cosine distribution of the O-H .... O hydrogen bond angle (denoted here as φ) and the O-O .... O angle θ formed by two neighboring O atoms around the central O atom. The comparison of these distributions in the different regions and in bulk water, shown in Fig. 3b, demonstrates clearly that the hydrogen bonding structure of the neighboring molecules is not affected noticeably by the interface, even in region III.

Relative orientation of the neighboring water molecules.

We have analyzed the influence of the interface on the relative orientation of two neighboring water molecules. Two molecules are regarded as neighbors if the distance of their O atoms is smaller than 3.3 Å (i.e., the first minimum position of the O-O radial distribution function). We have calculated the cosine distribution of the φ0 angle of the two dipole vectors, the β0 angle of the two molecular planes (or normal vectors) and the γ0 angle of the two H-H axes in the three regions and in bulk water. Surprisingly, neither the distribution of cos φ0 nor that of cos β0 has been changed noticeably from bulk water to region III. The P(cos β0) distribution (shown in Fig. 3a) is not changed either from bulk water to region II, however, in region III the preference of the neighbors for a parallel orientation is stronger than in bulk water. This can be explained by the ordering effect of the interface. Namely, the fact that the water molecules in region III prefer to stay parallel to the interface, and the neighboring molecules have the same orientational preference, increases the probability that these molecules are oriented also parallel to each other. Similar ordering effect of the interface has been observed in fully hydrated lipid membranes.

We have also analyzed the influence of the interface on the hydrogen bonding structure of water. For this purpose, we have calculated the cosine distribution of the O-H .... O angle of the two H-H axes in the three regions and in bulk water. As is seen, in the interfacial region the obtained distribution goes through a maximum around 0, indicating that here the preferential orientation of the water molecules is parallel to the interface. Hence, the negative peak of the cos α profile between ±18 Å and ±12 Å solely shows that when deviating from their preferential parallel orientation, the water molecules preferentially orientation is parallel to the interface rather than to the aqueous phase. When analyzing the cos β<0.5> and cos γ<0.5> profiles it is seen that the former has a pronounced positive, whereas the latter a negative peak in regions II and III. Since, contrary to P(cos α), the P(cos β) and P(cos γ) distributions (not shown here) are monotonous functions in all the three separate regions, the interpretation of these profiles are rather straightforward. Positive values indicate preferential parallel, whereas negative values preferential perpendicular orientation to the interface normal. Thus, the present results clearly show that in region II as well as in most parts of the interface the water molecules are preferentially oriented parallel to the interface. It is also seen that below ±12 Å, where the density of water is less than 15% of its bulk value, the orientational preference is slightly changed. Here the H-H vector is preferentially perpendicular to the interface, whereas the molecular normal vector has no orientational preference any more. This preferential orientation is similar to what has been found by Benjamin.
Interfacial structure from SCF and MD models

The density profiles obtained by the SCF and MD models were nearly identical with those obtained by MC. MD showed the characteristic water fingering described by Benjamin.

SCN⁻ ion at the water/DCE interface

From the MC results we calculated the cosine distribution of the angle \( \psi \) formed by the vector pointing from the S to the N atom of the SCN⁻ ion adsorbed at the interface and the vector perpendicular to the interface and pointing to the aqueous phase. For this analysis, only those configurations have been taken into account in which the SCN⁻ ion had at least one close contact water and one close contact DCE neighbor. In such configurations the SCN⁻ ion is indeed located at the boundary of the two phases.

The obtained distribution is shown in Fig. 4. As is seen, the SCN⁻ ion strongly prefers to point towards the aqueous phase with its N atom, whereas the S atom stays preferentially in the DCE phase. However, the present result should only be regarded as preliminary, and should be interpreted with caution, since, at the beginning of the simulation the SCN⁻ ion has been placed to the interface by pointing towards the aqueous phase with its N and towards the DCE phase with its S atom. Thus, the obtained preference can also be a reminiscent of the starting configuration, if the potential barrier of this rotation of the SCN⁻ ion is too high. The further investigation of this point needs to perform a set of new simulations, in which the starting position of the SCN⁻ ion is different from what has been done here (e.g., pointing towards the aqueous phase with the S atom, laying in the plane of the interface, etc.). Work in this direction is currently in progress.

Fig. 5 Difference between the fraction of SCN⁻ ions (in layer z) pointed with the N atom towards the organic phase and those with the N towards water. (Interface of exchange membrane and 0.1 M KSCN aqueous solution)

Summary and conclusions

MC simulation of the dichloroethane/water interface gave good agreement with MD results of Benjamin³ and with our MD calculations. The orientation of SCN⁻ ions at the interface could be calculated both by MC and SCF. SCF gave very many data that need further discussion. MC (and MD) cannot deal yet with dilute electrolytes. They are also too slow and expensive for applications where many systems need to be analyzed and compared, as in our case.

References

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