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The Binary System Formamide and Benzyl Alcohol Studied by Means of Computer Simulation

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Chemical reactions taking place in liquid surfaces and liquid / liquid interfaces are mainly based on structure and dynamics on the microscopic scale. In our group different experimental techniques are applied for achieving these properties: besides conventional methods for gaining macroscopic details (e.g. surface tension) a spectroscopic approach is used for information on a molecular level.

This spectroscopic technique and experimental results which motivated the computer simulation are outlined.

The present article deals with a binary liquid mixtures without miscibility gap namely formamide (FA) and benzyl alcohol (BA). It is examimed how experimental results can be supplemented by the simulation especially how much orientational and dynamical properties of one substance are altered by the presence of a second liquid.

Many computer simulations examine bulk properties whereas we follow a special strategy to create a liquid lamella with two interfaces liquid / vacuum. Thus one has the opportunity to study molecular properties for different surroundings, the bulk liquid and the surface exposed to vacuum.

In the following sections we first describe the experimental results and computer simulations that have already been carried out. For a detailed description the reader is referred to Ref. 1.

1 Introduction

Characterization of liquid surfaces based on the knowledge of composition of the surface region, molecular orientation and the kinetics of adsorption processes is main part of our experimental effort.

Besides classical experiments like surface tension measurments we apply spectroscopic methods to gain system parameters on a molecular length scale.

Electron spectroscopy is an established tool to study solid surfaces. Its high surfaces sensitivity of only several Å is based on small mean free path of the emitted photo electrons. Since the pioneering work in the early 70th[2] electron spectroscopy (X-ray Photoelectron Spectroscopy XPS, ESCA) was used for studying liquid surfaces. In 1986 MIES (Metastable Induced Electron Spectroscopy) using a projectile beam of excited helium atoms was established as absolute surface sensitive type of electron spectroscopy[3].

As usual one method can not reveal all information about a system. Electron spectroscopy for example averages over a certain time and sample volume. We thus carry out MD simulation to accompany our experimental findings.

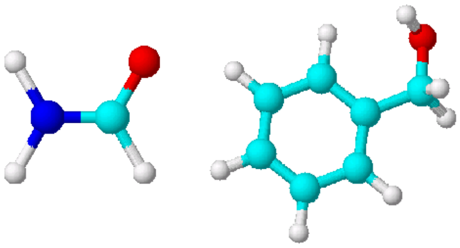


Figure 1. The two molecules simulated: Formamide (fa) on the left hand, benzyl alcohol (ba) to the right.

2 Motivation for the Simulation Due to Experimental Results

We investigated the system formamide (FA) and benzyl alcohol (BA) both with electron spectroscopy and with tensiometry finding that BA is the surface active component.

MIES reveals a preferential orientation in the liquid surface for both species: FA lies mainly flat in the time average whereas BA exposes the benzenes ring to vacuum. See Ref. 1 for further details.

3 Special Features for Simulating Liquid Surfaces

A large amount of computer simulation carried out deals with bulk properties. Macroscopically extended systems can in principle be studied by use of three dimensional boundary conditions handling a simulation box of typically a few 100Å edge size.

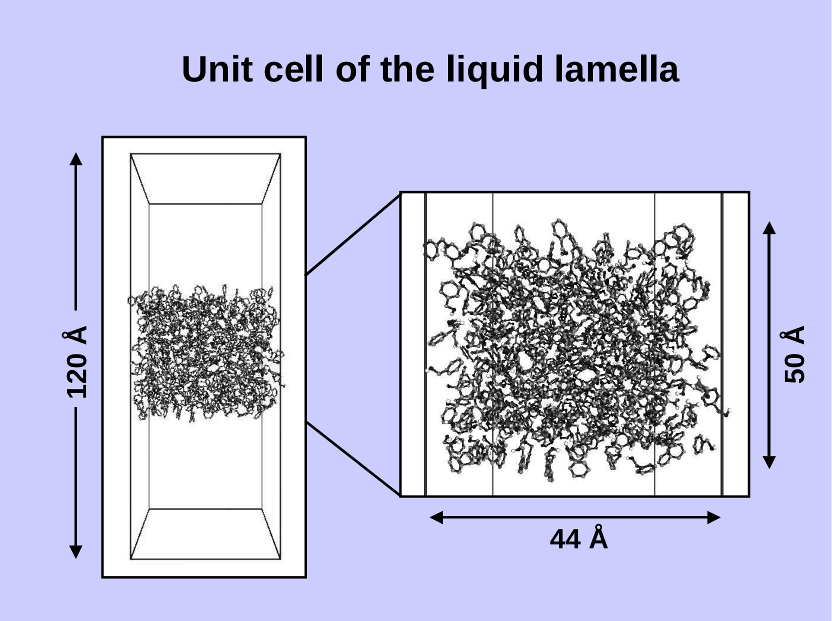


Figure 2. Schematic picture of the boundary conditions used: The simulation box is elongated in Z-direction in order to create 2 surfaces liquid / vacuum.

For our simulation of liquid surfaces a somewhat different approach must be used (fig. 2): we use a non cubic simulation box being elongated in Z-direction (the later surface normal). A liquid slab is then centered in Z and periodically continued in X- and Y-direction. The Z-size is chosen large enough to avoid interaction between the actual simulation box and its copy below and above.

4 Classical MD Simulation Results

4.1 Introduction

The results of our simulation using classical MD are outlined in the following section. Parameters of the different systems are listed in table 1. For comparison simulation for both pure liquids and for the mixture were performed[5, 6, 9].

molecular parameters				
	name	formular	sites	number
ensemble 1:				
species 1	benzyl alcohol	$C_6H_5CH_2OH$	9	420
species 2	formamide	$HCONH_2$	5	80
ensemble 2:				
species 1	benzyl alcohol	$C_6H_5CH_2OH$	9	420
species 2	formamide	$HCONH_2$	5	40
TD ensemble:				
species 1	benzyl alcohol	$C_6H_5CH_2OH$	9	108
species 2	formamide	$HCONH_2$	5	1

simulation parameters				
program	computer	knots	Box X,Y,Z [Å]	timestep $[fs]$
DL-POLY	CRAY T3E Jülich	32	44, 44, 120	2
	local workstation	1		

run parameters	
simulated time $[ps]$	temperature $[K]$
2300	300
3100	320

Table 1. MD-simulation benzyl alcohol + formamide, parameters.

4.2 Binary System Formamide and Benzyl Alcohol

In the experiment BA shows a strong preferential ordering of the benzyl alcohol in the surface and a surface potential of several hundred mV. This is supported by the simulation, the calculated surface potential being $350mV$. The simulation confirms the experimental results concerning the orientation of surface molecules. Thus sign and magnitude are in accordance with the experimental work.

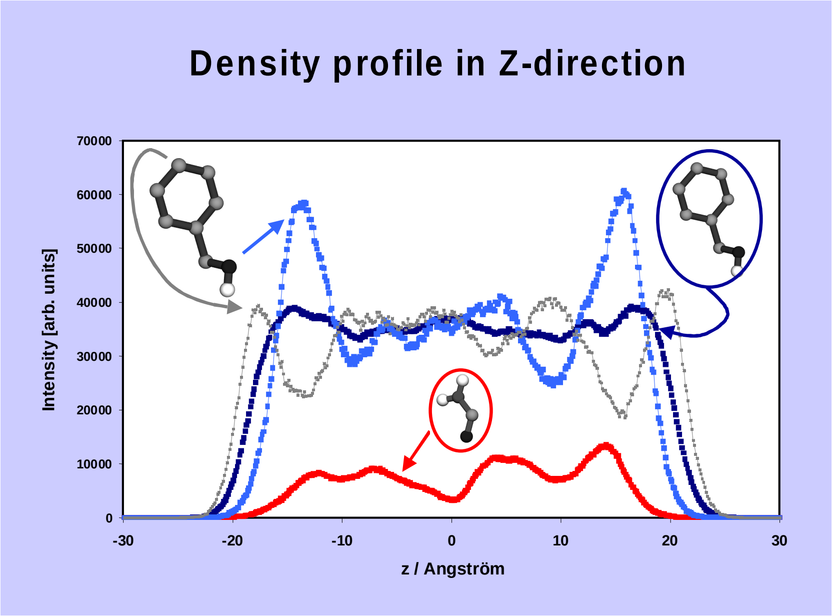


Figure 3. Density profile for the binary system formamide / benzyl alcohol. The preferential orientation of the benzyl alcohol can be seen: the benzene ring is exposed to vacuum while the O-H-group points towards the bulk of the liquid.

For pure formamide the simulation shows that on the average the molecular plane is oriented perpendicular to the liquid surface with N and O pointing towards the liquid bulk and the CH-group exposed to vacuum. Furthermore it could be seen that the liquid structure is dominated by a H-bonded network reaching from bulk into the surface region. For the binary system BA-FA we find that features of the pure component are less changed by the second liquid. Density profiles are shown in fig. 3.

4.2.1 The Influence of Temperature

The simulations were carried out for differnet temperatures both for the ensemble with a high amount of FA (80 molecules) an for the case of only 40 FA molecules. The angle between the Z-axis (surface normal) and the vector connecting the two opposite ring carbons as shown in figure 4 is taken as measure for the molecular orientation of the benzyl alcohol. Furthermore the diagramm 5 reveals the preferential orientation for BA molecules exposed to vacuum: The set of curves shifted vertical for a better overview refered to different surroundings of the molecules taken in to account. The lowest set belongs to the surface and the higher one goes the more we look into the bulk.

The more or less horizontal line demonstrates that the probability of all cosine values of the angle considered is the same. Therefore we find a random orientation of the ring independant of temperature. This behaviour obviously changes when approaching the surface: the cosine values show a clear preference at the left hand side. An indication for the ordering of the BA rings at the interface liquid - vacuum.

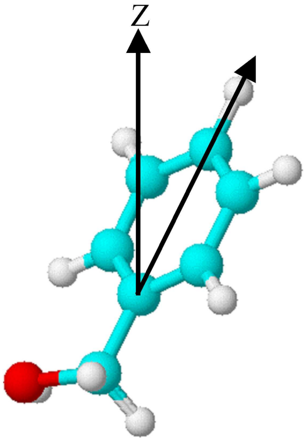


Figure 4. Schematic picture of the geometry used for studying the BA orientation. One vector is composed by two opposite carbon atoms and lies in the plane of the ring, the other one is the surface normal (Z-axis).

The results are plotted in fig. 5 making clear that there is no major influence for different temperatues choosen and for the two molar fractions use (420-80, 420-40).

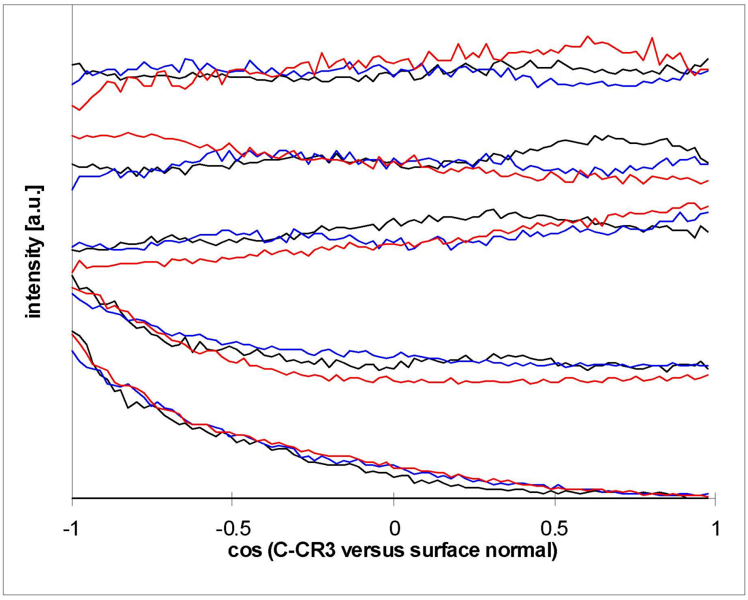


Figure 5. Temperature dependence of the ring-orientation and its variation depending on the position of the respective molecules: The three curves in one set belong to different temperatures and molar fractions. The sets are shifted vertically for clearness. In the upper pannel the lines are more or less horizontal meaning that all cosine values have the same probability. The ring is therefore randomly oriented. These curves belong to BA molecules in the bulk. The lowest set of curves shows a clear enhancement for negative cosine values: the BA ring has a preferential orientation in the surface. There is only minor temperature influence.

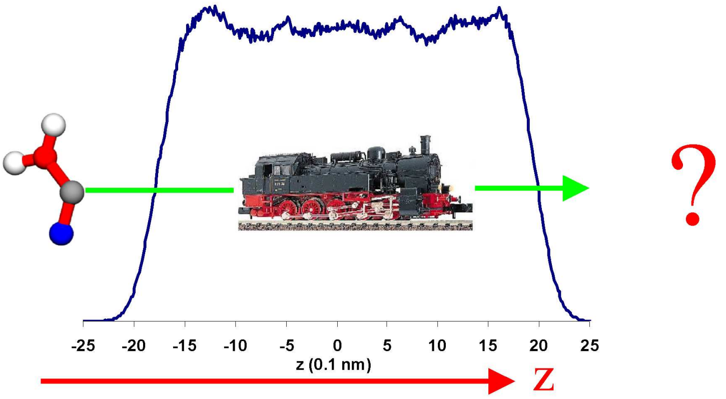


Figure 6. The idee of targeted dynamics: an additional force in Z-direction slightly moves the molecule through the liquid slab. Depending on the position one can monitore different properties like the respective energy and orientation.

5 The Use of Targeted Dynamics (TD)

5.1 General Remarks

Even nowadays computer simulation deal with the general restriction of a limited number of interaction sites and the small time interval accessible.

Segregation processes studied experimentally need $msec - sec$ depending on the surfactant used whereas classical MD methods are capable of covering a time regime of several $100ps$ up to a few ns meaning that diffusion itself can not be monitored. For handling this obstacle we therefore choose a different strategy, illustrated in fig. 6: Instead of waiting until molecules diffuse to a certain place of interest (in our case the interface liquid / vaccum) we slightly force the molecule in the desired direction. This method is called targeted dynamics (TD)[7]. In GROMOS this can be carried out by an additional so called gravitatonal force in Z-direction. The strength of that force and therefore the speed of movement can be varied. Of course one has to be careful that the molecular surrounding is not affected to much.

5.2 The Experimental Background for the TD Simulation

In the binary liquid system formamide-bencyl alcohol the alcohol is the surface active component. Even for low molar fractions of BA in the bulk it starts to form an overlayer on top of the formamide. For a certain concentration this overlayer is uncomplete and exposes holes in which formamide molecule can be embedded.

There are experimental findings[4] show that the embedded formamide shows a preferential orientation: Since the bencyl alcohol exposes a certain ordering in the surface this result in a net dipole moment. The orientation of FA is determined by that dipole moment.

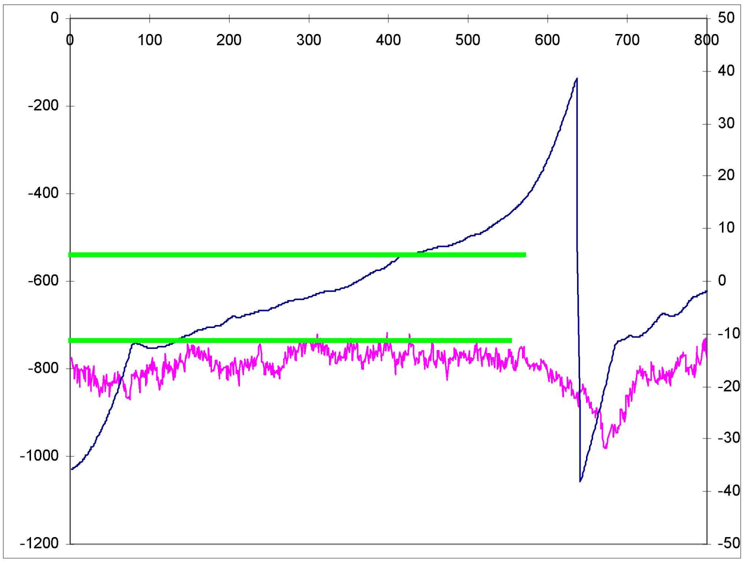


Figure 7. A typical TD run: The X-axis is the simulation time, the right Y-axis is the Z coordinate of FA. The blue curve is the trace the FA Z-coordinate from below the slab. The parabolic course due to acceleration in vacuum is observed. The green bars symbolize the benzyl alcohol. The move through the BA slab is slower than in vaccum due to surrounding molecules. After leaving the slab at the upper interface FA reaches the upper edge of the simulation box (roughly 40 Å) and undergoes a jump in z due to periodic boundary conditions.

5.3 TMD Simulation Results

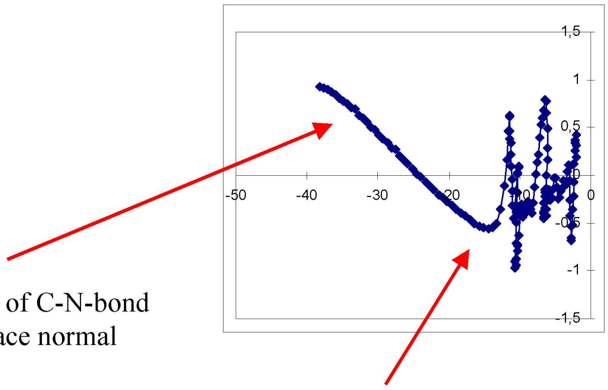
For the TD simulation we used an ensemble consisting of 108 BA molecules and one single formamide. The BA forms a slab similar to the simulations described in the first part of the present article. It is treated with classical MD without additional forces. The formamide is the species that has to undergo the additional driving force in Z-direction.

A typical run is outlined in fig. 7: The X-axis is denoted with the time of the simulation, the right Y-axis shows the Z coordinate of the moved formamide. The diagramm yields two types of information: the blue curve is the trace of the formamide. It starts in the left corner below the liquid BA slab. One can see the parabolic course when it is accelerated in vacuum. The green bar symbolizes the lower surface of the benzyl alcohol. The move of FA is obviously hindered. It is at first repelled and then slowly finds its way through the slab. After leaving the BA liquid at the upper interface with vacuum an accelerated movement starts again. After reaching the highest Z coordinate (roughly 40 Å) there is jump in Z due to periodic boundary conditions.

The red curve is a trace of the energy of the formamide. One can see that it shows a week minimum when entering the slab especially for the second time.

In order to compare the simulation with the above mentioned experimental results we furthermore looked at the formamide orientation when approaching the BA slab. This is drawn in fig. 8:

The X-axis now denotes the Z-coordinate of the formammide. So it approaches the BA slab again from the lower side of the simulation box. The Y-axis shows the cosine of the



Orientation of C-N-bond versus surface normal

Fa molecule turns into „right“ orientation when approaching the BA slab.

Figure 8. The diagramm shows how the formamide molecule orients when approaching the BA slab. When coming closer to the surface the influence of the BA dipole moment forces the molecule to orient according to the experimental findings.

angle between the C-N bond of the FA in respect to the surface normal.

The diagramm must be read as follows: the FA approaches the BA with a certain orientation. As soon as it feels the influence of the BA dipole moment it changes its orientation in order to fit into the BA surface in the right fashion.

The respective orientation is in accordance with the experimental findings mentioned above.

6 Some Comments and Outlook

The described targeted dynamics simulation introduced in Ref. 7 has already been tested for the adsorption of thiol molecules at a gold surface[8] and in a first simple run for a formamide molecule through a slab of benzyl alcohol[9]. In the latter case it was seen that simulation parameters where choosen in a fashion that the system was muddled by the additional force. For the study shown in the present article we pic up the knowledge gained so far and try to apply the new technique more reasonable by tuning the parameters. Tracing the total energy of the respective molecule under constrains gives a handle on preferred orientations and positions. For making use of that energy the GROMOS source code has to be changed or additional programms have to be developed. In the long run it is planned to use this *targeted dynamics* algorithm for more complex systems.

Acknowledgments

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