Free Energy of Alkanol Transfer from Water to Oil

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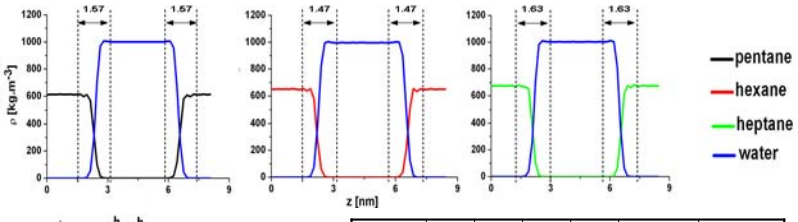
ABSTRACT

Detailed knowledge of the interfacial phenomena can contribute significantly to the rational practical application of small amphiphiles in electrochemistry, extraction, stabilization of emulsions or drug design. Surfactant behavior in the heterogeneous oil-water formulations is known to differ distinctly from the one observed in bulk water or oil or at the gas-liquid interface.

The first stage of our approach consists of classical Molecular dynamics simulations of models of pure water-oil interface. Mass density profiles, interfacial tension, electrostatic potentials, and thickness of the surface layer are estimated, and show reasonable correspondence to published data. Static configurations from these simulations are then taken as model systems, where a single alkanol molecule is inserted. The free energy (PMF) profile for transfer of an alkanol across the interface is obtained from umbrella sampling calculations, followed by WHAM analysis. Comparison of the results with thermodynamic data for the adsorption energy and partition coefficient of alcohols at the water-alkane interface is made to assess the accuracy of the model.

STRUCTURAL FEATURES



System	h_1 [nm]	h_2 [nm]	w_c [Å]	w [Å]	γ [mN.m^{-1}]	γ_{exp} [1,2] [mN.m^{-1}]
pentane	2.33	2.39	1.44	1.56	53.01 ± 0.21	48.74 - 50.8
hexane	2.21	2.27	1.36	1.49	53.97 ± 0.10	50.38 - 51.25
heptane	2.09	2.16	1.35	1.52	64.05 ± 9.42	50.71 - 51.64

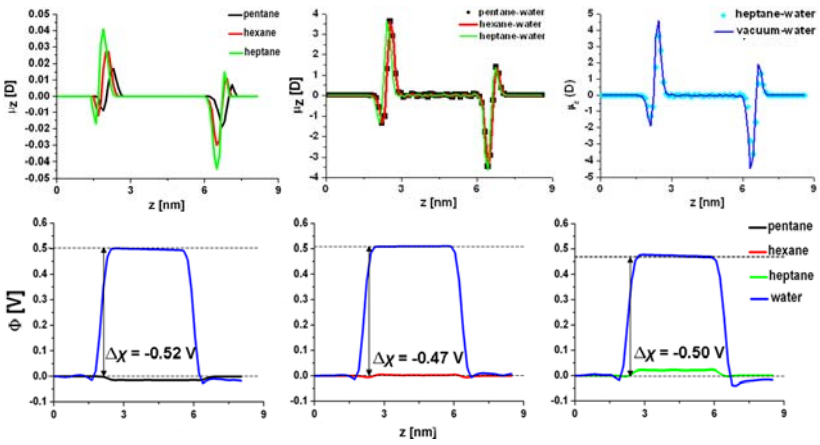
$$w^2 = w_c^2 + w_o^2$$

$$w_o \approx |h_1 - h_2|$$

h_1, h_2 – W|O Gibbs dividing surfaces position, w – interfacial thickness, w_c – capillary contribution to w, γ – interfacial tension

Top: mass density profiles along the z-axis; Bottom : fit[3] of the simulation data (left) and table with structural parameter values (right)

ELECTRIC PROPERTIES



Top: μ_z – component profiles along the z-axis for the three alkanes (left) and water (center). The latter are compared with simulation data from a water–vacuum system (right). Bottom : the electrostatic potential in the system as a function of z.

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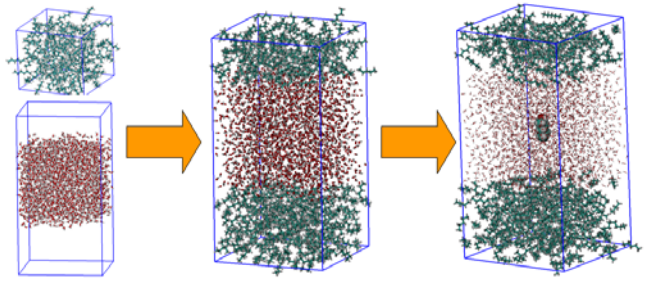
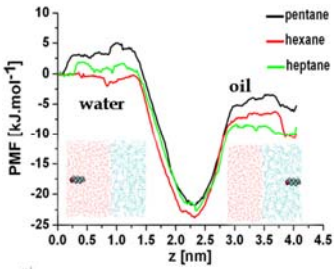
COMPUTATIONAL DETAILS

1) **Oil-water systems: AMBER99 force field for alkanes, TIP4P water model, NPT ensemble (P = 1 atm, T = 298 K), PBC, LRC for energy and pressure, 2 fs time step, 30 ns MD trajectory.**
2) **Umbrella potential, k = 1500 kJ.mol^{-1}.nm^{-2}; position restraints on the alcohol**

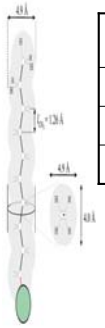
MOLECULAR MODELS



FREE ENERGY OF TRANSFER OF PENTANOL



PMF between the centers of mass of the pentanol molecule and the water layer (left). Values of the free energy of transfer from water to interface (W-I), from interface to oil (I-O), and from water to oil (W-O) are listed in the table below.



System	$\Delta G_{W\to I}$ [kJ.mol^{-1}]		$\Delta G_{I\to O}$ [kJ.mol^{-1}]		$\Delta G_{W\to O}$ [kJ.mol^{-1}]	
	calc	exp[4]	calc	exp[4]	calc	exp[4]
pentane	-24.79	-24.27	17.08	34.59	-7.71	10.32
hexane	-23.23	-24.27	15.98	34.59	-7.25	10.32
heptane	-23.40	-24.27	12.91	34.59	-10.41	10.32

$$\ln K_p = \ln K_p^o - \frac{n_A \mu_A}{RT} + \frac{n \Delta\mu_{CH_2}}{RT}$$

$$\Delta\mu_{CH_2}^{calc} = \frac{dPMF}{dz} l_{CH_2}$$

System	dPMF/dz [kJ.mol^{-1}. Å^{-1}]	l_{CH2} [Å]	$\Delta\mu_{CH2}$/RT	
			calc	exp[5]
pentane	3.27	1.26	1.66	1.39
hexane	3.15	1.26	1.60	1.39
heptane	2.97	1.26	1.51	1.39

Top: empirical model used to describe K_p as a function of alkyl chain length and approximated formula used to calculate $\Delta\mu_{CH2}$. Bottom : comparison of the PMF derivatives with experimental data.

CONCLUSIONS

❖Good estimates of the interfacial tension and thickness.

❖Strong polarization effects in the boundary region, reasonable shift of the electrostatic potential.

❖ Calculated free energies are close to the experimental ones, poor description of interface-to-oil transition.

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