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Short Communication

Length Dependence of Demixing and Micelle Formation in a Model for Tenside-Water Mixtures

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Abstract. — Monte Carlo simulations of a Larson-type model for oil-water-amphiphile mixtures determine the characteristic micelle concentration CMC and the oil-water phase separation temperature $T_c$. These data agree partially with experimental data on aqueous solutions of the non-ionic tensides $\text{CH}_3(\text{CH}_2)_{1-j}-(\text{O}-\text{CH}_2\cdot\text{CH}_2\cdot\text{O})_j\text{H}$

Microemulsions of oil, water and amphiphiles have been simulated successfully on lattices with various approximations like the Widom model [1]. Even more realistic are off-lattice molecular dynamics studies [2]. Numerically in between are Larson-type models [3] where amphiphilic self-avoiding chains are dissolved in an Ising solvent on a cubic lattice. These Monte Carlo simulations have shown [4] that the CMC (characteristic micelle concentration) decays exponentially with increasing length of the hydrophobic tail of the amphiphilic chains. It is the aim of this study to compare simulations with experimentally determined “critical” micelle concentrations (CMC) and phase separation, as a function of both head and tail size. In particular, experiments with non-ionic tensides of the type

$\text{CH}_3\cdot(\text{CH}_2)_{1-j}-(\text{O}-\text{CH}_2\cdot\text{CH}_2\cdot\text{O})_j\text{H}$

dissolved in water reveal a characteristic dependence of the demixing temperature on the ratio $i/j$. That means it is found experimentally that for $j = 3$ to 8 and $i = 6$ to 12, the demixing temperature $T_c$ is roughly the same for different $i$ and $j$, provided the ratio of $i/j$ is the same.

We used the model of reference [4], without a head-head repulsion, but with a head containing more than one site. Thus the whole amphiphilic chain on the simple cubic lattice consists of $j$ consecutive hydrophilic head sites, followed by $i$ hydrophobic tail sites. The hydrophilic monomers are represented by Ising spins 1, the hydrophobic ones by Ising spins $-1$. These chains reptate like slithering snakes in the solvent represented again by Ising spins $+1$ (water) and $-1$ (oil); in binary mixtures without oil, all solvent sites are $+1$. The interaction between nearest neighbors is taken into account in an (apart from the chain reptation) standard Glauber
simulation at temperature \( T \), using lattice sizes from \( 50^3 \) to \( 600^3 \) and up to 30,000 reptation attempts per chain.

The CMC is defined [4] here as that volume concentration of amphiphilic chains at which half of the chains are isolated and in equilibrium with the other half of the chains assembled in micelles, i.e. in clusters of two or more adjacent chains. The CMC is not a "critical" concentration in the sense of a sharp phase transition.

Figure 1 shows the experimental [5] as well as the simulated CMC's for tail sizes \( i = 6 \) and 8, for various head sizes \( j \). We see that the slight increase of the experimental CMC with increasing head length \( j \) is very well reproduced by the simulation. However, the exponential decay of the CMC with increasing tail length \( i \) is stronger in the experiments than in the simulation. (This discrepancy also appears for \( i = 12 \), not shown in this Fig.).

The experimental tenside solutions show a lower critical temperature, an effect not explained by the present model. Therefore, instead we simulated the oil-water demixing temperature [6] \( T_c \) at a fixed volume concentration of ten percent polymer chains. Indeed, we found that for a fixed \( i/j = 1 \) the six critical temperatures for \( j = 2 \) to 7 all were near \( 4.0 \pm 0.2 \) in units of \( J/k_B \), where \( J \) is the Ising interaction energy. For \( i/j = 2 \) and \( j = 2, 3, 4 \) the transition temperature went down to \( 3.2 \pm 0.1 \). At \( i + j = 12 \), it was about 2.3, 2.7, and 3.4, respectively, for \( j = 2, 3 \), and 5. (Without amphiphilic chains, \( T_c = 4.51 \).) The experimental critical temperatures, for \( i = 6, 8, 10, 12 \) and \( j = 3, 4, 5, 6, 8 \) follow roughly a straight line \( T_c = 404 - 43 i/j \) K and thus decrease about half as fast with increasing \( i/j \) as the simulated values. Thus the computer model follows qualitatively but not quantitatively the experimentally observed trends as a function of head and tail size. This dependence on \( i/j \) only has to be contrasted with the temperature where the amphiphilic chains separate out of the solvent for \( i = 1 \); there the demixing temperature increases roughly linearly [7] with the chain length \( i + j \).
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References


