

STATISTICAL, NONLINEAR,
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The Critical Crossover at the *n*-Hexane–Water Interface

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Abstract—According to estimates of the parameters of the critical crossover in monolayers of long-chain alcohol molecules adsorbed at the *n*-hexane–water interface, all systems in which this phenomenon is observed are characterized by the same value of the critical exponent $\nu \approx 1.8$.

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Atoms or molecules adsorbed on the surface of a liquid or crystal frequently form a spatially inhomogeneous structure in which domains of two homogeneous phases coexist [1–4]. Both of these phases tend to intermixing, since the formation of one-dimensional interphase boundaries leads to a significant decrease in the system energy [5]. An evident consequence of this is the impossibility of a two-dimensional (2D) first-order phase transition in this system; instead, an infinite sequence of phase transitions (critical crossover) must take place [6].

This article presents the results of an analysis of experimental data obtained earlier [7, 8], which allowed a critical parameter of the crossover at the *n*-hexane–water interface to be established.

A macroscopically flat interphase boundary (interface) between *n*-hexane (a nonpolar organic solvent) and water (see Fig. 1) offers an example of the system, featuring the phenomenon of critical crossover. Under normal conditions, *n*-hexane (saturated hydrocarbon with the formula C_6H_{14} , a density of $\sim 0.65 \text{ g/cm}^3$ at $T = 298 \text{ K}$, and a boiling temperature of about 342 K) and water exhibit virtually no mutual solubility.

It was reported earlier [7–9] that a surface electrical double layer can form at the *n*-hexane–water interface owing to adsorption (from hexane solutions) of long-chain molecules of fluorinated alcohols, such as 1,1,2,2-tetrahydroheptafluorodecanol ($FC_{10}OH$) and 1,1,2,2-tetrahydrohencosafluorododecanol ($FC_{12}OH$), or saturated monatomic alcohols, such as *n*-tetracosanol ($C_{24}OH$) and *n*-triacontanol ($C_{30}OH$) [7–9]. The fluorocarbon chain of $FC_{12}OH$ is longer by two $-CF_2-$ units than that of $FC_{10}OH$, and the hydrocarbon chain of $C_{30}OH$ is longer by six $-CH_2-$ units than that of $C_{24}OH$. The main difference between the properties of fluorocarbon and hydrocarbon chain molecules is their flexibility. Indeed, the former molecules at room temperature can be considered absolutely rigid rods, whereas the latter are susceptible to conformation isomerization.

Synchrotron radiation reflectometry data show that molecules of the aforementioned substances at sufficiently low temperatures adsorb from a solution in liquid hydrocarbon at the *n*-hexane–water interface in the form of a monolayer (Gibbs monolayer) with a certain set of thermodynamic parameters (p , T , c). It was found that the long-chain molecules of various alcohols are ordered differently on the water surface. The density of molecules in the condensed low-temperature phase of monolayers of fluorinated alcohols is close to the density of the corresponding volume crystals, whereas the density of the condensed phase of saturated monatomic alcohols is close to that of the high-molecular-mass hydrocarbon liquid. These alcohols are nearly insoluble in water at room temperature.

As the temperature T is increased at normal pressure ($p = 1 \text{ bar}$), the monolayer exhibits a transition from the condensed to the gaseous phase. The transition temperature T_c is determined by the alcohol concentration c in the volume of the organic solvent (a reservoir for surfactant molecules). By analogy with 3D systems, we can say that the monolayer of a fluorinated alcohol exhibits a solid–gas transition, while the

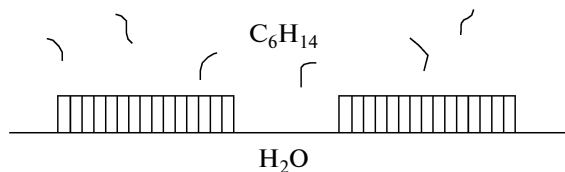


Fig. 1. Schematic diagram of a macroscopically flat interface between *n*-hexane (a light nonpolar organic solvent) and water, which is oriented by the gravitational field. Under normal conditions, *n*-hexane and water are immiscible solubility. In a broad temperature range, domains of the condensed low-temperature phase in the monolayer of adsorbed alcohol (vertical rectangles) coexist with domains of the gaseous high-temperature phase and both occur in equilibrium with the volume phase of the organic solvent, which serves as a reservoir for surfactant molecules.

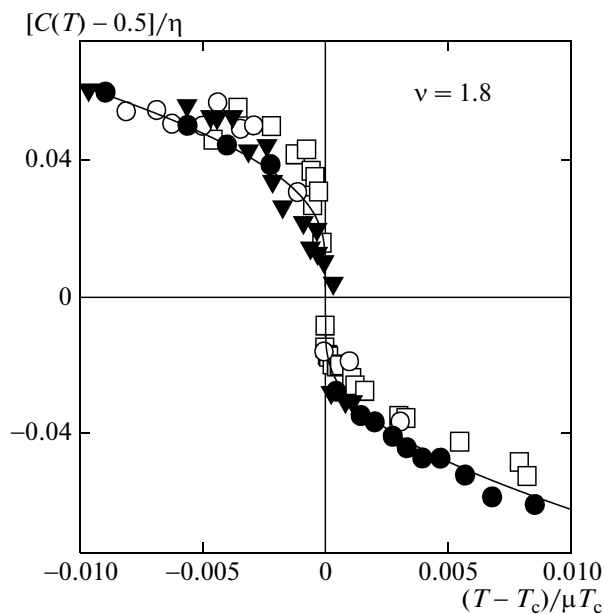


Fig. 2. Temperature dependence of the surface fraction $C(T)$ occupied by domains of the low-temperature condensed phase of alcohols at the n -hexane–water interface. Symbols represent experimental data [7, 8] for $C_{24}OH$ (filled circles) and $C_{30}OH$ (open circles) and fluorinated alcohols $FC_{10}OH$ (squares) and $FC_{12}OH$ (triangles); the solid curve shows the results of calculations using Eq. (1) with $\nu = 1.8$.

monolayer of a saturated monatomic alcohol exhibits a transition from liquid (amorphous monolayer) to gas.

However, there are several experimental facts evidence the existence of a spatially inhomogeneous equilibrium structure on the surface in the vicinity of T_c [2, 7]. At fixed p and c , the surface exhibits coexistence of the domains of condensed and gaseous phases in a rather wide temperature interval. Thus, the density and organization of domains in the adsorbed layer gradually change in a wide (more than 5 K) tempera-

Parameters of critical crossover in monolayers of long-chain alcohol molecules adsorbed at the n -hexane–water interface

Alcohol	T_c , K	η	μ
$C_{24}OH$	300.0	8.0 ± 1.0	1.0 ± 0.5
$C_{30}OH$	302.5	8.5 ± 0.9	1.6 ± 0.6
$FC_{10}OH$	300.7	9.0 ± 1.0	7.0 ± 1.0
$FC_{12}OH$	314.0	8.0 ± 1.0	1.1 ± 0.5

Note: Critical exponent in Eq. (1) is $\nu = 1.8$. Data for $FC_{10}OH$ and $C_{30}OH$ were obtained using the incoherent reflection model, while those for $FC_{12}OH$ and $C_{24}OH$ were obtained using the coherent reflection model. Errors in determining parameters η and μ were established in terms of the standard χ^2 criterion on a 0.9 confidence level.

ture interval, rather than exhibit a jump at T_c (as it would be for the first-order phase transition).

The fractionation and intermixing of surface phases in the electric double layer at the liquid–liquid interface are possible due to competition between long- and short-range interactions [5, 10]. On the one hand, the electrostatic energy of the linear boundary between two phases with different surface polarizations exhibits a negative logarithmic singularity (because its electric field decays with distance r according to the $\propto 1/r$ law), which favors unlimited intermixing of these phases. On the other hand, a short-range interaction of van der Waals nature determines the energy of linear tension γ_l (i.e., the energy of phase boundary formation with neglect of the logarithmic effect). The stabilization of the spatially inhomogeneous (fractal) structure on the surface in a certain vicinity of T_c , where the surface energy of the condensed phase is comparable with the energy of the gas phase, takes place due to the finiteness of $\gamma_l > 0$ (e.g., $\gamma_l \sim 3 \times 10^{-11}$ N in a monolayer of $FC_{12}OH$ [11]).

Marchenko [10] described the so-called “devil’s staircase” of phase transitions with an accumulation point at T_c in the system under consideration. In the limit of a large number of phase transitions, surface fraction $C(T)$ occupied by the domains of the low-temperature condensed phase varies according to the following law:

$$C(T) - C(T_c) = \eta \operatorname{sgn}(T_c - T) \left(\ln \frac{\mu T_c}{|T_c - T|} \right)^{-\nu}, \quad (1)$$

where $T \rightarrow T_c$ and η , μ , and ν are constant phenomenological quantities. The identical equality $C(T_c) \equiv 0.5$ determines transition temperature T_c . The product μT_c is a parameter that determines the region of existence of the spatially inhomogeneous surface structure, η characterizes the molecular properties of the system, and exponent ν must be a universal parameter.

Figure 2 shows good agreement between the $C(T)$ dependences determined in [7, 8], on the one hand, and relationship (1) with the parameters listed in the table, on the other hand. In contrast to estimations obtained earlier [7, 8], this relationship between the theoretical parameters of the critical crossover in monolayers of alcohols at the n -hexane–water interface allows all systems in which this phenomenon is observed to be described using the same critical exponent $\nu = 1.8 \pm 0.4$. Then, μ is in fact the single parameter that can vary in relation (1), since the value of η is also the same (to within the given error) for all systems under consideration. The latter circumstance is apparently due to the fact that the dipole moment of the molecules of all alcohols is determined primarily by the presence of a hydroxy group.

In conclusion, it should be noted that relationship (1) can also be used for description of the critical crossover in Gibbs monolayers of alcohols during variation of the external pressure p at $T = \text{const}$ [12, 13].

In this case, C is considered as a function of external pressure p .

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