SURFACE ADSORPTION AND ORIENTATION NEAR THE CRITICAL POINT OF BINARY LIQUID MIXTURES[1]

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ABSTRACT

The noncritical liquid/vapor surface is completely saturated with the component of smaller surface tension for sufficiently large surface tension difference between the two components of a critical liquid binary mixture. This complete (or strong) adsorption is described by a universal scaling function of the volume fraction order parameter. We have determined the universal function *P*; the models provide excellent descriptions of the ellipsometric data for a number of weakly polar and nonpolar binary liquid mixtures. In the limit of a small surface energy, the surface preference, however, depends strongly on the strength of the surface field and the surface is no longer completely saturated. We also studied the universal function *G* for this weak critical adsorption using a homologous series of critical liquid mixtures where their surface tension difference changes from negative to positive as the length of the carbon chain increases. The experimental results agree with theoretical predictions in both one- and two-phase regions. In addition to the surface adsorption, we will also discuss a dipole orientational order at the liquid/vapor surface of highly polar + nonpolar mixtures. Consideration of an electrostatic model provides a reasonable description of this effect.

KEY WORDS: adsorption; critical phenomena; ellipsometry; surface orientation.

1. INTRODUCTION

In this paper, we present a study of the critical phenomena associated with the noncritical liquid/vapor interface of critical binary liquid mixtures focused especially on critical adsorption and dipole surface orientational order.

Two decades ago, Fisher and de Gennes [1] predicted the existence of preferential adsorption. Motivated by their innovative prediction, numerous theoretical and experimental studies have made a big progress in determining bulk and surface universal constants and functions. Further substantial progress has been made by the research presented here, in experimentally determining universal scaling functions for strong and weak critical adsorption, and even in discovering an additional surface orientation produced by the highly polar component within a mixture.

1.1. Bulk Critical Phenomena of Binary Liquid Mixtures

We consider the thermophysical properties of binary liquid mixtures composed of two non-reacting components. First of all, let us think of a mixture that consists of A (lighter) and B (heavier) components. Then, they are mutually soluble at sufficiently high temperatures in general, but separate out into two phases when the temperature falls down below the transition temperatures of the mixture. The separated bulk phases are called α and β for convenience corresponding to A rich and B rich phases, respectively.

The transition temperature, at which a system changes from one phase into two phases, varies with the bulk volume composition of the mixture. By measuring the transition temperatures against the volume fraction of A (or B) component in bulks, one can experimentally obtain a coexistence curve. For a given mixture, when the temperature of the system crosses the coexistence curve from either the upper or lower side, a phase transition occurs discontinuously. However, it is possible to find a critical composition, say, critical volume fraction v_c such that the volume fraction of A in the α phase gradually approaches that of A in the β phase until they exactly match at the critical temperature T_c. This continuous transition point is called a *critical point*.

The shape of the coexistence curve is symmetric around the critical point (v_c, T_c) and universal for a variety of systems such as binary mixtures, pure fluids, binary alloys, ferromagnets, etc., belonging to the *Ising universality class* [2]. If we define a normalized temperature, so-called, reduced temperature $t = |T - T_c| / T_c$, the volume fraction difference of component A between in the α and β bulk phases is given by

$$\begin{aligned} \Delta v \propto v_A - v_c &= 0 && \text{for one-phase region} \\ &= M_t^{\beta} && \text{for two-phase region} \end{aligned} \tag{1}$$

in terms of t where the coefficient $M_$ is a system dependent constant describing the shape of the coexistence curve while the exponent β (= 0.328) is a universal constant [3].

Within the bulk of a critical mixture, the local volume fraction fluctuates considerably around T_c. According to the classical phenomenological (Landau) theory, the bulk free energy of a critical AB mixture can be expressed roughly in a parabolic shape. Even though

the mean field theory fails near a critical point, where the size of the volume fraction fluctuations becomes much larger than the molecular size, it still provides a basic idea about how the local fluctuation grows as T approaches T_c. In the vicinity of T_c, because the free energy curve becomes flatter, it requires only a relatively small thermal energy fluctuation to create large volume fraction fluctuations comparing to the temperature regime sufficiently far from T_c. As the critical temperature is approached, the size of the local fluctuations increases and finally diverges at the critical point. This divergence is described by the (bulk) correlation length

$$\xi = \xi_o t^{-\nu} \tag{2}$$

where the critical exponent ν (= 0.632) is another universal constant and the coefficient ξ_o is a system dependent constant.

2. CRITICAL ADSORPTION

At boundary surfaces of mixtures, preferential adsorption of the component with the smallest surface tension occurs. Even in a pure liquid with a small impurity, the surface may be dominantly occupied by a couple of molecular layers of the impurity component if it is surface active. When this preferential adsorption occurs at the boundary surface of a critical AB liquid mixture, the adsorption profile structure is simply described by a universal function and the phenomenon is called a critical adsorption.

Critical adsorption is distinguished from noncritical adsorption by the size of the adsorbed film thickness and by its universal behaviour. Because of the large adsorption thickness ($\sim \xi$) compared with the size of molecules, critical adsorption should be described as a function of depth rather than by averaging over the composition throughout the interface. To describe the critical adsorption of component A at the liquid/vapor interface, we define an order parameter as a volume fraction deviation from the critical volume fraction v_c, i.e., $m(z) = v_A(z) - v_c$ where $v_A(z)$ is the volume fraction of component A at depth z.

In binary liquid mixtures, critical adsorption is controlled by the surface energy h_1, hence the order parameter describing the interfacial structure is now given by

$$m(z) = M_t^{\beta} G(x, y) \tag{3}$$

where $G(x, y)$ is a universal scaling function, $x = (z + z_e)/\xi$, $y = h_1 t^{-\Delta_1}$, Δ_1 (= 0.461) is a surface exponent, and z_e is a system dependent extrapolation length [4].

Neglecting critical finite size effects [5], which become dominant in the limit of a thin film between two boundaries, universal function G must describe all crossovers from strong to weak critical adsorptions controlled by the surface field h_1 (≈ Δσ) where Δσ (= σ_A - σ_B) is the surface tension difference between components A and B. Although strong adsorption is more common in nature, it occurs when $|h_1| >> 0$ while weak adsorption occurs only in the limit of a small surface field ($h_1 \approx 0$). For simplification, we can redefine the universal

function in the saturated limit as $P(x)$ by removing the surface energy dependent parameter y since h_1 quickly saturates in this limit, namely, $G(x, y) \to P(x)$ as $y \to \infty$. In Fig. 1, we compare strong adsorption with weak adsorption via their representive universal functions, P and G, respectively. While the volume fraction at the surface in the strong surface energy limit is saturated at its maximum value, $v_A(z=0)=1$, the surface value of G for weak adsorption is proportional to the surface energy h_1. This surface energy dependency is valid only near the surface ($z \leq\sim |h_1|^{-\nu/\Delta_1}$; see Fig.1). In contrast, in the limit of $x \to \infty$, both scaling functions become identical again, i.e., $G(x, y) \to P(x)$ as $x \to \infty$.

Various theoretical methods, such as Monte Carlo Simulation (MC), mean field theory (MF), renormalization group theory (RG), and recently local functional theory (LF), have been used to study this universal function for strong critical adsorption. These theories only provide a qualitative or rough description for the experiments [4]. For example, MF provides a preliminary expectation of the universal constants and a preliminary shape of the universal function P while RG provides an asymptotic form of P leaving its coefficients undetermined. The universal functions P and G that we determined by ellipsometry will be discussed here.

2.1. Strong Adsorption

In the strong surface field limit ($|h_1| >> 0$) where the surface is occupied dominantly by the component with larger surface tension, the interface structure is given by

$$m(z) = M_t^{\beta} P(x) \tag{4}$$

from Eq. (3). The universal function P for the strong adsorption of a number of different weakly polar [4] and nonpolar [6] critical mixtures has been determined by using the optical reflection technique of ellipsometry, simply as

$$P_<(x) = \begin{pmatrix} 0.788 \\ 1.117 \end{pmatrix} x^{-\beta/\nu} + \begin{pmatrix} -0.245 \\ 0.169 \end{pmatrix} x^{(1-\beta)\nu} \quad \text{for } x \leq 1.15\text{, and}$$

$$P_>(x) = \begin{pmatrix} 0 \\ 1 \end{pmatrix} + \begin{pmatrix} 0.963 \\ 0.572 \end{pmatrix} e^{-x} + \begin{pmatrix} 1.437 \\ 0.533 \end{pmatrix} e^{-2x} \quad \text{for } x \geq 1.15\ , \tag{5}$$

ignoring higher order terms where the coefficients in the first (second) row stand for one- (two-) phase region. A comparison between Eq. (5) (dashed lines) and experimental ellipticity data $\bar{\rho}$ (open symbols) in one-phase region for four mixtures is shown in Fig. 2a where $\bar{\rho} = \mathrm{Im}(r_p / r_s)|_{\theta_B}$ at the Brewster angle θ_B with r_i the complex reflection amplitude for polarization i [7].

2.2. Weak Adsorption

In Eq. (3), the universal function that describes weak adsorption can be expressed as

$$G(x, y) = P(x)Z(x, y)\,. \tag{6}$$

The G function is more general than P because it must describes the adsorption profile with any surface field h_1, including weak adsorption where $h_1 \to 0$. The G function has been studied by systematically changing the second variable y, using a homologous series of critical mixtures. Here component B (= methyl formate) is fixed while component A is varied by choosing the n-alkanes (from undecane (denoted C11) to tetradecane (C14)). For these particular systems, h_1 varies continuously from a negative to positive value with increasing n-alkane chain length. Here $h_1 = 0$ occurs at C12.6. The ellipsometric determination of crossover function Z has resulted in

$$Z(x, y) = (1 - e^{-\varsigma})^{\Delta_1/\nu}\,, \tag{7}$$

especially in one-phase region, where $\varsigma \sim x|y|^{\nu/\Delta_1}$ and surface critical exponent $\Delta_1 = 0.46$. For two-phase region, the crossover function has been also determined but in a more complicate form [8]. The solid lines in Fig. 2b compare Eq. (7) with experimental ellipticity data (solid symbols) for our critical mixtures [8,9]. Significant departure is found between experimental data and the strong adsorption behaviour of Eq. (5) (dashed lines).

Another exciting finding during this weak adsorption experiment was that the noncritical liquid/vapor interface of C13 and C14 undergoes a critical wetting transition as T_c is approached from the lower temperatures, as expected by Cahn's theory [10]. While the metastable $\bar{\rho}$ data were used for the analysis of weak adsorption above, the stable data have been converted into the thickness of the wetting films using a slap model. The results [11] are consistent with the mean field theory [12]. The insets in Fig. 3 show the time scans of the $\bar{\rho}$ data, where the average of each metastable state (circled around symbols) represents adsorption data (circled). Here, we need to note that the shape of the $\bar{\rho}$ curves for wetting differs by temperatures (insets).

3. SURFACE ORIENTATION OF HIGHLY POLAR LIQUIDS

In addition to the preferential adsorption, one (or both) component(s) of the mixture may prefer to align in a particular direction at the liquid/vapor interface of an AB liquid mixture if the component is polar. This surface orientation of dipolar molecules has been studied. We consider that B component is highly polar but A component is non-polar, with a large surface tension difference $\Delta\sigma(=\sigma_A - \sigma_B << 0)$, so that the polar (B) molecules, in the vicinity of the interface, prefer to lie parallel to the liquid/vapor surface while being strongly desorbed from this interface. The qualitative features of this dipolar orientation can be understood by considering a simple electrostatic interaction generated between a dipole and its image dipole.

Consider a dipole with dipole moment p, which is situated just below a sharp boundary separating a liquid (α) phase from a vapor (v) phase, where these phases possess the static dielectric constants of ε_α and ε_v, respectively. An image dipole is induced in phase v with

effective dipole moment p_v of magnitude $p_v = p(\varepsilon_\alpha - \varepsilon_v)/(\varepsilon_\alpha + \varepsilon_v)$ (Fig. 4 inset). The interaction energy between p and p_v is now given by

$$U = p^2 \frac{(\varepsilon_\alpha - \varepsilon_v)(1+\cos^2\theta)}{(\varepsilon_\alpha + \varepsilon_v)d^3} \tag{8}$$

where d is the distance between the dipoles, and θ is the angle between the dipole direction and the z axis (normal to the surface). In order to minimize the potential energy, the real dipole at the liquid/vapor interface where $\varepsilon_\alpha > \varepsilon_v$ preferentially orients parallel to the interface.

This electrostatic model provides only a qualitative picture of the dipole induced orientational order. In practice, the situation is far more complicated because the liquid/vapor interface is never sharp but instead possesses a thickness ξ where the local volume fraction also varies with position. The local volume fraction of dipolar molecules with orientation θ at position z can be written as [13]

$$v(z,\theta) \sim v(z)(1+\alpha_2(z)(3\cos^2\theta - 1)) \tag{9}$$

in the absence of any external field. Here, the position dependent parameter $\alpha_2(z)$ describes the variation in orientational order with depth. Surprisingly, experiments indicate that

$$\alpha_2(z) \sim [m(z)]^2 . \tag{10}$$

However, a theoretical explanation for this interrelationship between the local volume fraction and the local orientational order is still lacking. Good agreement is found between Eq. (10) and experimental data for the highly polar mixtures; 2-nitroanisole + cyclohexane (Fig. 4, solid line) and 4-nitroanisole + cyclohexane [14]. In Fig. 4, the dashed line indicates the predicted behaviour in the absence of any orientational order (i.e., $\alpha_2(z) = 0$).

4. SUMMARY

Using ellipsometric technique, we have successfully determined the universal functions for critical adsorption in the function of z. The P function provides an excellent description of strong adsorption profiles for a number of weakly polar and nonpolar mixtures (Fig. 2a). The G function for weak adsorption has been estimated from a homologous series of n-akanes + methylformate mixtures and is also applicable to the strong adsorption profiles. Here, an appropriate question that may arise in a practical situation is when the surface energy becomes saturated. The crossover point of the surface energy can be easily estimated by investing the G function. The result shows that, when the surface tension difference $|\Delta\sigma|$ becomes larger than ~6 erg/cm^2, the surface field must be saturated completely so that the P function becomes fully functional on describing the adsorption profiles at all accessible temperatures.

For highly polar mixtures, the adsorption profiles are no longer isotropic, and thus one must consider the interfacial orientation in addition to the adsorption. Especially for critical of a nonpolar (A) and highly polar (B) mixtures where the polar component is desorbed at the liquid/vapor interface, the orientational order is proportional to the square of local volume fraction (Eq. (10)). As a result, the long-ranged dipole–image dipole repulsion stretches the adsorption profile and the dipoles prefer to orient parallel to the surface. These observations are still not fully understood but are consistent with an electrostatic consideration.

In summary, by systematically controlling variables via a number of critical AB liquid mixtures, we have examined critical adsorption and surface orientation, and estimated the universal functions describing the interfacial profile structure of the noncritical liquid/vapor surface. Although the technique of ellipsometry provides exceptionally high depth resolution less than 0.05 nm, some other techniques (e.g., X-ray or neutron reflectometry) must be employed in order to fully verify the universal functions. An understanding of these fundamental scientific issues will have important implications on various related fields, such as, surface physics, chemistry, biology, etc.

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Figure captions:

Fig. 1. Schematic diagram of strong (dashed line) and weak (solid line) critical adsorption in the function of depth. Note that exponent $\kappa = (\Delta_1 - \beta)/\nu \sim 0.21$.

Fig. 2. (a) Strong adsorption for dodecane + tetrabromoethane (DT) [6], aniline + cyclohexane (AC), isobutric acid + water (IW) and lutidine +water (LW) [4]. The *P* function (dashed lines) handles well the critical adsorption for the binary liquid mixtures (symbols) with large $\Delta\sigma$. (b) Weak adsorption for the homologous series of mixtures, methyl formate + n-alkane [8,9]. The solid lines are calculated from Eq. (7). The dashed line depicts the C11 to C14 dependency, if strong adsorption was present, in the limit of positively saturated surface field ($h_1 > 0$). Note that this figure concerns only one-phase region ($T > T_c$) and that the deviation of $\overline{\rho}$ with different mixtures in (a) are due to having various optical dielectric constants while the deviation in (b) is mostly caused by the variation of the h_1 field.

Fig. 3. Weak adsorption in one- and two-phase regions for tetradecane (C14). The calculated curves (Eq. (7)) fit well the ellipsometric data both in one- (solid symbols) and two-phase (open symbols) regions. For two-phase region, the adsorption data were averaged from the metastable data (e.g., circled regions in the insets). The metastable adsorption lasts a few hours or less, depending upon the reduced temperature *t*. The insets represent the $\overline{\rho}$ data against time at three different temperatures.

Fig. 4. Strong adsorption, in the presence of dipole orientational order, for the highly polar mixture 2-nitroanisole + cyclohexane [14]. Our model (Eq. (6), solid line) is in agreement with the $\overline{\rho}$ data (symbols). The dashed line represents the predicted dependency in the absence of orientational order. The inset illustrates a dipole (arrow) – image dipole (dashed arrow) repulsive interaction at the surface.

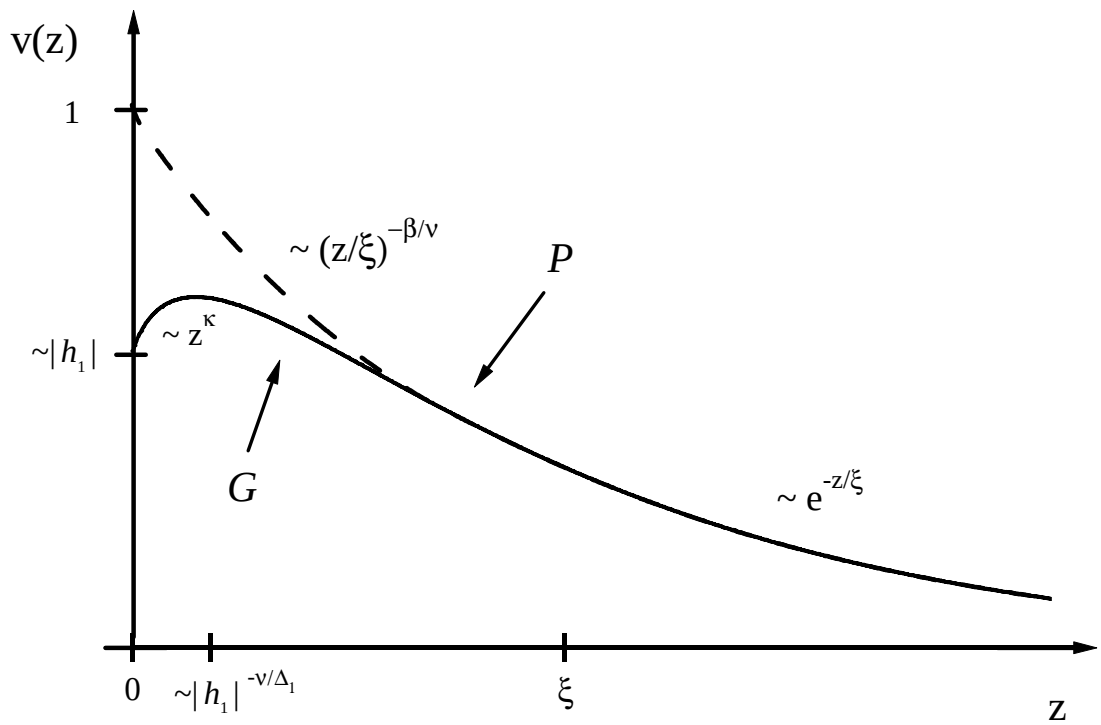


Fig. 1

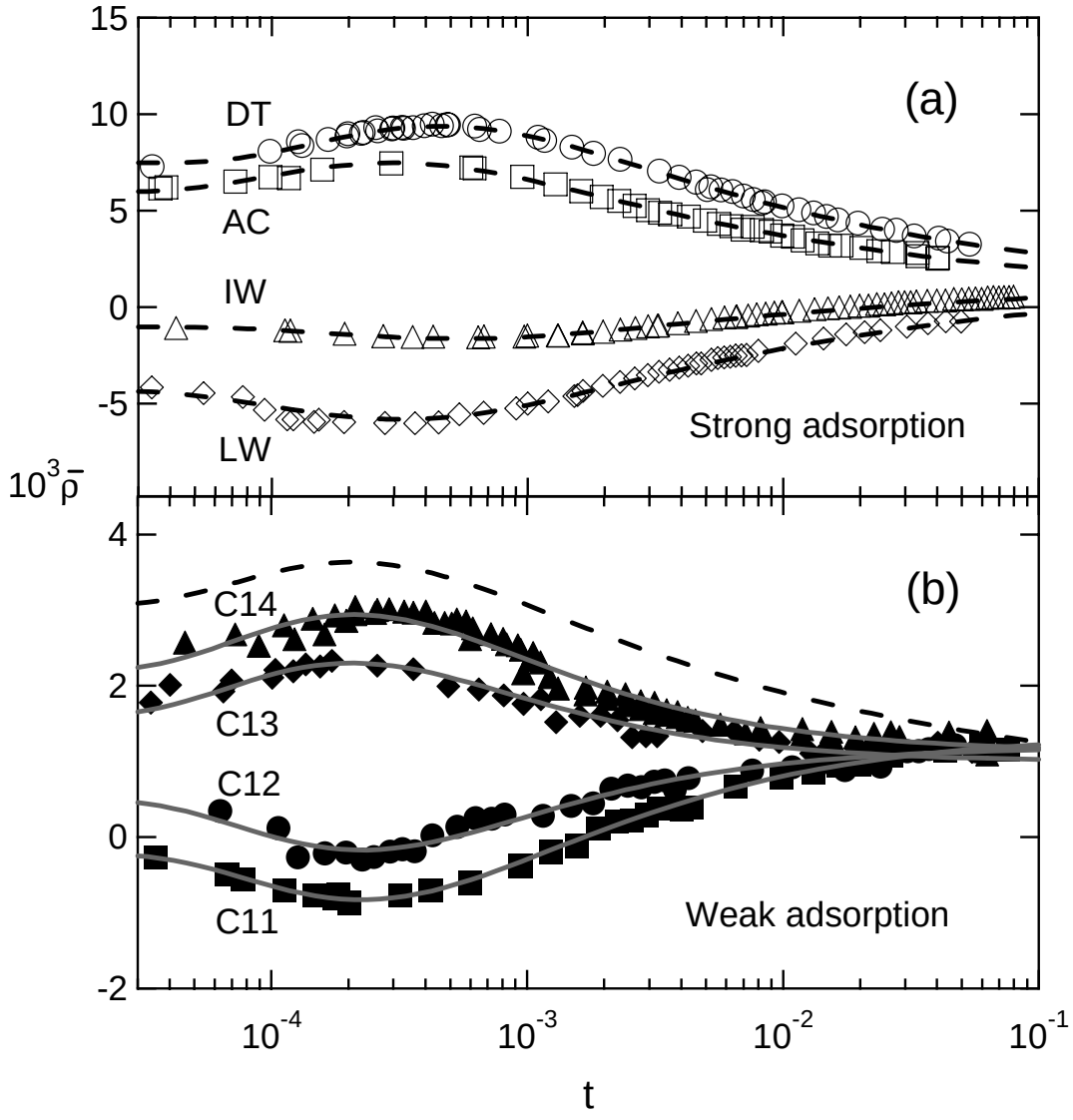
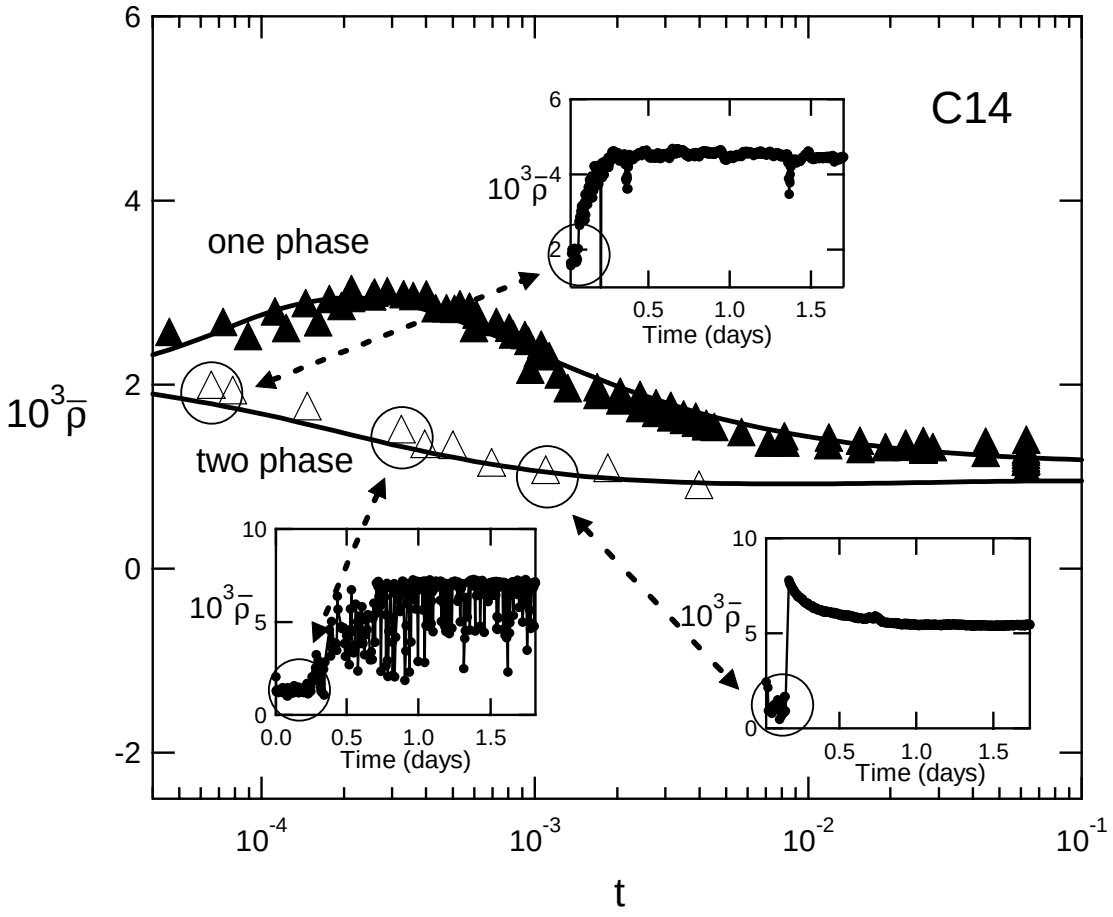

15
10
5
0
-5
DT
AC
IW
LW
(a)
Strong adsorption
$10^3\bar{\rho}$
4
2
0
-2
C14
C13
C12
C11
(b)
Weak adsorption
10^{-4}
10^{-3}
10^{-2}
10^{-1}
t

Fig. 2


C14
one phase
two phase
$10^3\bar{\rho}$
t
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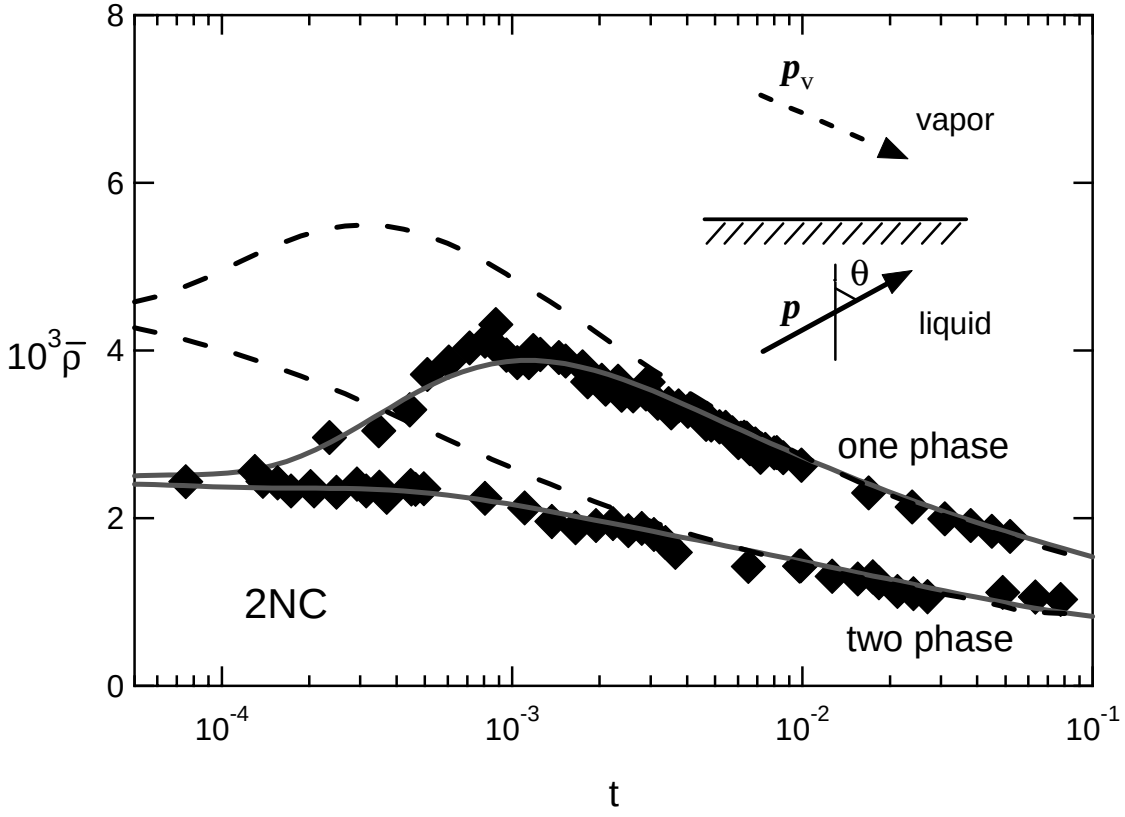
$10^3\bar{\rho}_5$
Time (days)

Fig. 3


8
6
4
2
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p_v
vapor
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Fig. 4