Transitional behaviour of amphiphiles
at the air/water interface under equilibrium
and dynamic conditions

Abstract According to an earlier hypothesis of one of us on the
surface equation of state, extended-chain surfactants usually adsorb in
(at least) two different surface configurations depending on the surface
area available per adsorbate molecule. Evidence for the continuous
transition between the different surface configurations in the equilibri-
un state is provided by thermodynamic (surface tension), rheological (surface elasticity as
measured by surface laser light scattering) and electric (surface
potential) surface properties of surface chemically pure amphiphiles.
The transition between the two alternative surface configurations was
also observed in surface potential kinetics of n-dodecanoic acid in
0.005 M HCl.

Key words Adsorption isotherm · Surface configuration · Decanoic
acid · Surface tension · Surface dilational elasticity

Introduction

To describe the equilibrium, dynamic, kinetic, and rheological properties of surfactant adsorption layers
one first needs a convenient surface equation of state to
enable the bulk concentration to be related to the surface
excess. To do so the equations of Langmuir–Szykowskii
and of Frumkin [1–3] have always been used for
describing either “ideal” or “real surface behaviour”,
obviously satisfactorily.

However, only since the advent of “surface-chemical
purity”, enabling one to provide and to guarantee
sufficient surfactant purity not only for the bulk but also
for the interfacial phase, have doubts arisen.

When we tried to describe the equilibrium surface
tension ($\sigma_e$) versus concentration ($c$) isotherms of various
homologous series of amphiphiles we realized that you
cannot match these isotherms satisfactorily using either of
these equations when you cover the entire adsorption
interval.

Therefore the idea was put forward to take into
consideration different surface configurations of the
adsorbed amphiphile depending on the grade of its
surface coverage [4]. To do so we assumed that the
adsorbates’ surface configuration can occur in two
alternative kinds: a flat arrangement at comparatively
low surface coverage and a (more or less) upright
configuration at high surface densities. According to
this, the transition from the low to the high surface
coverage configuration does not occur as an all-or-
nothing change but occurs successively within a definite
concentration interval the width of which depends on the
amphiphile’s geometric conditions. This interval is called
the “transitional region”.

In fact, this hypothesis led to a much better matching
of the experimental $\sigma_e$ versus $c$ isotherms. By using it, any
experimentally determined $\sigma_e$ versus $c$ isotherm can be
matched with high precision. The whole $\sigma_e$ versus $c$
isotherm is described mathematically by the sum of two
contributions according to Eq. (1)

$$\Delta \sigma_e(c) = x \Delta \sigma_e^1 + (1 - x) \Delta \sigma_e^2 .$$

$\Delta \sigma_e^1$ represents the Traube–Henry equation,

$$\Delta \sigma = kc = RT \gamma ,$$
and $\Delta \sigma^\text{HI}$ stands for the Langmuir–Szyszkowski equation,
\[
\Delta \sigma = RT \Gamma_{\infty} \ln(1 + c/a_L)
\]
and/or the Frumkin equation
\[
\Delta \sigma = -RT \Gamma_{\infty} \ln \left(1 - \frac{\Gamma}{\Gamma_{\infty}}\right) + d' \left(\frac{\Gamma}{\Gamma_{\infty}}\right)^2,
\]
with
\[
d' = \Gamma_{\infty} H^p
\]
and
\[
c = a_L \Gamma / (\Gamma_{\infty} - \Gamma) \exp(-2H^\Gamma / RT \Gamma_{\infty}).
\]
$\Gamma_{\infty}$, $a_L$, and $H^p$ denote the saturation adsorption, surface activity, and surface interaction parameters, respectively.

The transitional region is described by the function $\alpha(c)$, which is equal to 1 at the onset and equal to 0 at the end of the transitional interval. The transition function is defined by
\[
\alpha = 0.5[1 - p(X_t)]
\]
with
\[
X_t = (\ln c - \ln c_i) / \beta,
\]
where $c_i$ and $\beta$ stand for the transition concentration (50% value) and the width of the transition range, respectively. Various transition functions, such as $\tan(c, \beta)$, $\tanh(c, \beta)$, or polynomials have been applied. We usually used the latter. The different transition functions do not change the transition in principle; however, the width of the transitional interval is somewhat dependent on the kind of the transition function (Fig. 1). The function $\alpha$ is determined by matching the experimental $\sigma_e$ versus $c$ isotherm using Eq. (1). This represents a nonlinear problem of minimization which is solved by an iteration procedure.

Meanwhile a lot of fundamental features of surfactant adsorption have been discovered by this approach, such as

1. A dependence of the homologous surfactants’ cross-sectional areas on chain length [5, 7, 8].
2. Even/odd effects of the adsorption parameters within homologous series of surfactants [5–8].
3. Discrete counterion effects [9].

Although this idea turned out to be so successful we were eager to look for more support from surface properties other than surface tension to learn about the nature of the transitional region.

The surface potential and laser light scattering seemed promising for observing changes in the adsorbate’s surface configuration.

![Fig. 1 Equilibrium surface tension ($\sigma_e$) and transitional function ($\alpha$) with respect to the concentration of $n$-decanoic acid in 0.005 M HCL. The dashed lines show extrapolations of the single Henry (right; $\alpha = 1$) and/or Frumkin (left; $\alpha = 0$) equation of the two-state approach to the surface equation of state [4] (cf. Eq. (1)). The dash-dot line represents the transition function, $\alpha(c)$](image)

**Experimental**

The surface tension was determined using an automatic Lauda Tensiometer, taking into consideration modifications necessary in applying it to surfactant solutions [10].

Stock solutions were purified by an automatically operating high-performance purification apparatus described in Ref. [11] to get “surface chemically pure” surfactant solutions. The grade of purity was monitored by applying the criterion derived in Ref. [12].

Surface potential ($\Delta V$) measurements were performed using the vibrating plate method (KSV 1000 SPD). The vibrating electrode (disk of 2-cm diameter and 0.5-mm thickness) operated at a frequency of 90 Hz.

The scattering of light by thermally excited capillary waves has become an accepted technique to probe the dynamic behaviour of liquid interfaces [13]. The laser light scattering experiments refer to the damping of thermally excited ripples occurring in the surface of every liquid with amplitudes of several angstroms. The surface of a liquid supporting an adsorption layer sustains various modes of fluctuation, which are excited by thermal excitation. Two are of present concern: capillary waves and dilatational waves. The former are primarily governed by the surface tension, $\sigma$, while the dilatational waves are subject to the surface dilatational elastic modulus, $E$. In principle, $E$ is equivalent to the Gibbs modulus; however, the surface waves are sensitive to surface properties appropriate to the frequencies of the capillary fluctuation, which may differ from their equilibrium values owing to relaxation processes, such as diffusional exchange and molecular reorientation in the adsorption layer.

The thermally excited capillary waves on a liquid surface can be studied by quasielastic light scattering. They are also coupled to the