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Author(s)	Lin, M; Firpo, JL; Mansoura, P; Baret, JF
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A phase transition of the adsorbed layer: High pressure effect on fatty alcohol adsorption at an oil-water interface

Michel Lin, Jean-Luc Firpo, Pierre Mansoura, and J. François Baret

Département de Physique des Liquides, Université de Provence, Marseille, France
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Measurement of the interfacial tension of fatty alcohol solutions permits determination of the amount of amphiphile adsorbed. This amount varies with both pressure and concentration. At some critical value, the interfacial solution splits into two phases. In the dilute phase, the adsorbed molecules are solvated by the oil whereas in the condensed phase there is no solvent interspersed between the aliphatic chains. A thermodynamical analysis of this two-dimensional phase transition is given assuming the interfacial solution to be regular.

I. INTRODUCTION

The interfacial properties of liquids, as all physico-chemical properties, depend on pressure and temperature conditions. There have been numerous studies on the variation of these properties, in particular the temperature dependence of interfacial tension.¹ In contrast, the pressure influence has received little attention with only a few studies reported in the literature. Most of these studies are concerned with the complex mineral oil-water system.²⁻⁴ Undoubtedly, this interest is attributable to practical ramifications in petroleum secondary recovery. Perhaps the most interesting work done in this field is the recently published paper⁵ describing experiments related to pressure effects on the adsorption of an amphiphile at a liquid/liquid interface. In the present study, a system very similar to that used by Motomura and collaborators⁵ is employed. However, by using a broader range of concentrations, we are able to obtain a result which is not apparent from their data, viz., a phase transition of the adsorbed layer. Of course, it is well documented that two-dimensional amphiphilic systems such as the air/water monolayer or the lipid bilayer may show phase transitions. The evidence we present in this work is, to the best of our knowledge, the first such evidence for a transition in the two-dimensional layer adsorbed at the liquid/liquid interface.

II. EXPERIMENTAL CONDITIONS

Interfacial tension was measured by the pendant drop technique. A beam of parallel and monochromatic light illuminates the drop. A camera with a large focal lens focused on the drop meridian gives a large size picture. The measure of two diameters on this picture yields the value of the interfacial tension.^{4,6} The precision of this measure is limited only by the diffraction fringe surrounding the drop, which leads to an error on the interfacial tension of about ± 0.2 mN/m.

To control the hydrostatic pressure, the drop is placed inside a high pressure chamber having two quartz windows. A complete description of this chamber is given elsewhere.⁷

The system studied is composed from water and a paraffinic oil solution of fatty alcohol. The paraffinic oil was purchased from Enzybio Laboratories under the

trade name of Parlax. It is purified in order to suppress any trace of surface active impurities. A good test of purification is given by the stability of interfacial tensions. In this oil is dissolved a defined amount of normal alcohol; we use the C₁₀, C₁₁, C₁₂, and C₁₃ alcohols, i. e., *n*-decanol, *n*-undecanol, *n*-dodecanol, and *n*-tridecanol, respectively. They are high grade products supplied by Flucka. The water is distilled three times. The experiments were done at 20 ± 0.1 °C.

III. RESULTS

We have measured the interfacial tension of systems composed of water and fatty alcohol solutions in paraffinic oil at various pressures and concentrations. In Figs. 1 and 2, interfacial tension γ is plotted as a function of pressure P at various concentrations for *n*-decanol and *n*-undecanol, respectively. These plots reveal three features worth noting: (1) the γ vs P curves appear linear within the pressure range studied; (2) the slope of these curves becomes progressively smaller as the concentration of alcohol increases; (3) for higher concentrations, there is a definite break in the slope of these curves (phase I and phase II: low and high slopes, respectively). For the longer chain alcohols (*n*-dodecanol and *n*-tridecanol), the γ - P graphs have similar features with the breaks occurring at lower concentration and lower pressure.

IV. DISCUSSION

The Gibbs-Duhem relation for the interfacial zone is⁸

$$S^\sigma dT - V^\sigma dP + \sum_{i=1}^3 N_i^\sigma d\mu_i^\sigma + A^\sigma d\gamma = 0 \quad (1)$$

The intensive variables T , P , μ_i^σ , and γ are the temperature, the pressure, the surface chemical potential of the species i , and the interfacial tension, respectively. The extensive variables S^σ , V^σ , N_i^σ , and A^σ are the surface entropy, the volume of the interfacial layer, the number of molecules i lying in the interfacial zone, and the interface area, respectively. At constant temperature, this expression can be rewritten in the following form

$$d\gamma = \frac{V^\sigma}{A^\sigma} dP - \sum_{i=1}^3 n_i^\sigma d\mu_i^\sigma \quad (2)$$

with

$$n_i^\sigma = N_i^\sigma / A^\sigma.$$

Indexing "1" the water, "2" the oil, and "3" the surface active substance, one has

$$(\partial\gamma/\partial P)_T = n_1^\sigma \delta v_1 + n_2^\sigma \delta v_2 + n_3^\sigma \delta v_3, \quad (3)$$

where δv_i stands for $(v_i^\sigma - v_i)$, the difference between the molecular volume of the species "i" at the interface and in the bulk. For the pure oil/water interface, Eq. (3) becomes

$$(\partial\gamma/\partial P)_T = n_1^\sigma \delta v_1 + n_2^\sigma \delta v_2. \quad (4)$$

Experimentally, we see in Figs. 1 and 2 that the slope of the γ - P curve is constant and positive in the case of the 1-2 interface. Since n_1^σ and n_2^σ are positive, this implies that (1) either $\delta v_1 > 0$ and $\delta v_2 > 0$, (2) or $\delta v_1 > 0$ and $\delta v_2 < 0$ with $n_1^\sigma \delta v_1 > n_2^\sigma \delta v_2$, (3) or $\delta v_1 < 0$ and $\delta v_2 > 0$ with $n_1^\sigma \delta v_1 < n_2^\sigma \delta v_2$. Because of the symmetrical character of the interface with respect to 1 and 2, it is likely that the first alternative is true. We will therefore assume $\delta v_1 > 0$ and $\delta v_2 > 0$. In other respects, this is compatible with the idea that the less attractive the environment, the larger the occupied volume.

For decanol (Fig. 1) and undecanol (Fig. 2), it is possible to study the pure fatty alcohol/water interface, since these substances are liquid at 20°C. In this case,

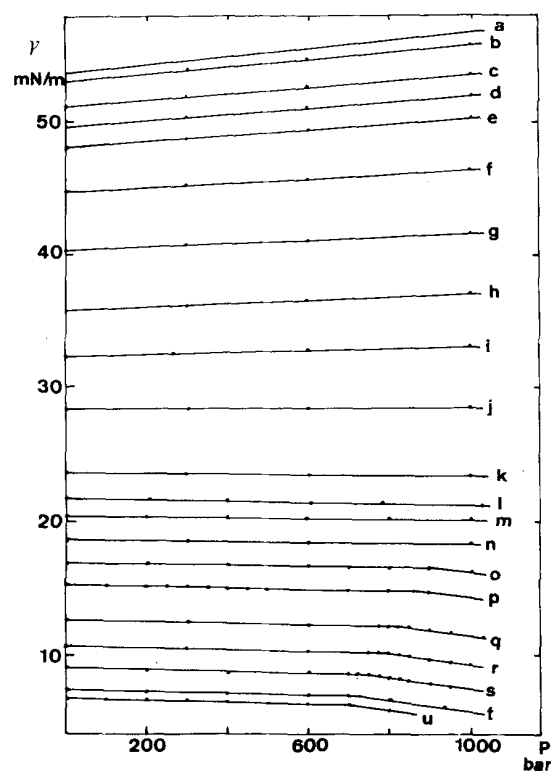


FIG. 1. Variation of the interfacial tension (γ) vs pressure (P) for a decanol solution/water interface at different concentrations (w/w): (a) zero, (b) 1/30000, (c) 1/10000, (d) 1/6000, (e) 1/4000, (f) 1/2000, (g) 1/1000, (h) 1/600, (i) 1/400, (j) 1/250, (k) 1/150, (l) 1/118, (m) 1/100, (n) 1/75, (o) 1/50, (p) 1/25, (q) 1/10, (r) 1/5, (s) 2/5, (t) 4/5, (u) pure decanol.

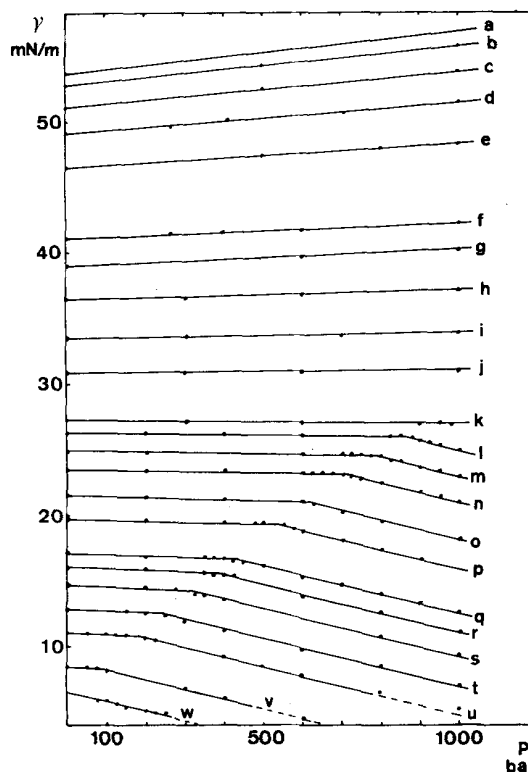


FIG. 2. Variation of the interfacial tension (γ) vs pressure (P) for an undecanol solution/water interface at different concentrations (w/w): (a) zero, (b) 1/30000, (c) 1/10000, (d) 1/5000, (e) 1/2500, (f) 1/1000, (g) 1/750, (h) 1/560, (i) 1/400, (j) 1/300, (k) 1/200, (l) 1/175, (m) 1/150, (n) 1/125, (o) 1/100, (p) 1/72, (q) 1/40, (r) 1/30, (s) 1/20, (t) 1/10, (u) 1/5, (v) 1/2, (w) pure undecanol.

$(\partial\gamma/\partial P)_T$ is negative, i. e. ,

$$n_1^\sigma \delta v_1 + n_3^\sigma \delta v_3 < 0.$$

Therefore, if $\delta v_1 > 0$, δv_3 must be negative. For an amphiphilic molecule, the interfacial environment is globally more attractive than in the bulk of the solution. The following signs:

$$\delta v_1 > 0, \quad \delta v_2 > 0, \quad \delta v_3 < 0,$$

suggest that the understanding of the changes in the slopes $(\partial\gamma/\partial P)_T$ for the water/solution interface is straightforward:

(i) In the first phase (I), the slopes of these curves decrease as the amphiphile concentration increases. However, when the concentration increases, n_3^σ increases (see Figs. 3 and 4), and consequently the term $n_3^\sigma \delta v_3$ eventually dominates over the other two terms.

(ii) In the second phase (II), the slope has the same value as for the pure surface active substance. This suggests that in phase II the solvent (2) is absent from the interfacial layer and only amphiphile and water remain at the interface. Hence, the transition point corresponds to a condensation of the adsorbed layer for a critical value of the surface concentration n_3^σ , (which depends on pressure and concentration); there is expulsion of the solvent from the interface with replacement by the surface active solute.

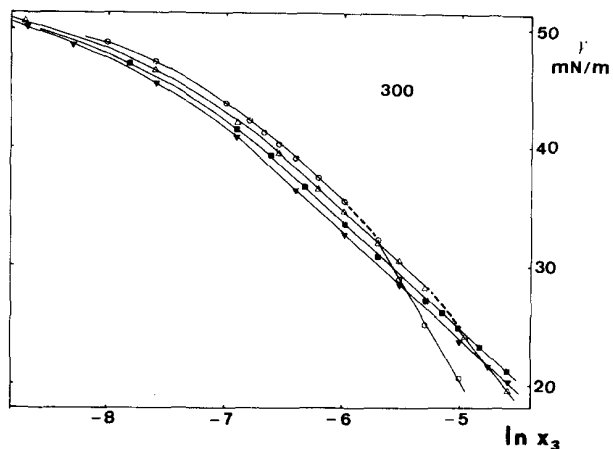


FIG. 3. Plot of interfacial tension variation versus the concentration logarithm at 300 bar for (▼) decanol, (■) undecanol, (Δ) dodecanol, (○) tridecanol.

The linearity of the γ - P curves is explained by the expression

$$\frac{\partial}{\partial P} \sum_i \frac{N_i^a}{A} (v_i^a - v_i) = 0. \quad (5)$$

Since the total number of molecules "i" is a constant $N_i^T = N_i^a + N_i = \text{constant}$, we may write

$$\frac{\partial V}{\partial P} - N_i^T \frac{\partial v_i}{\partial P} = 0. \quad (6)$$

Consider a system containing the same number of molecules i but without interface. Its volume would be

$$V^{wi} = \sum_i N_i^T v_i.$$

Expression (6) now becomes

$$\frac{\partial V}{\partial P} - \frac{\partial V^{wi}}{\partial P} = 0. \quad (7)$$

Therefore, the linearity of the γ - P curves implies that the system's compressibility is equal to that of a system without an interface.

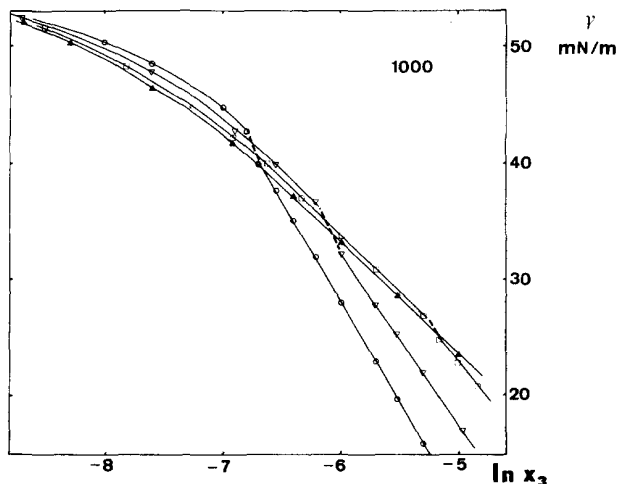


FIG. 4. Same as Fig. 3 but at 1000 bar.

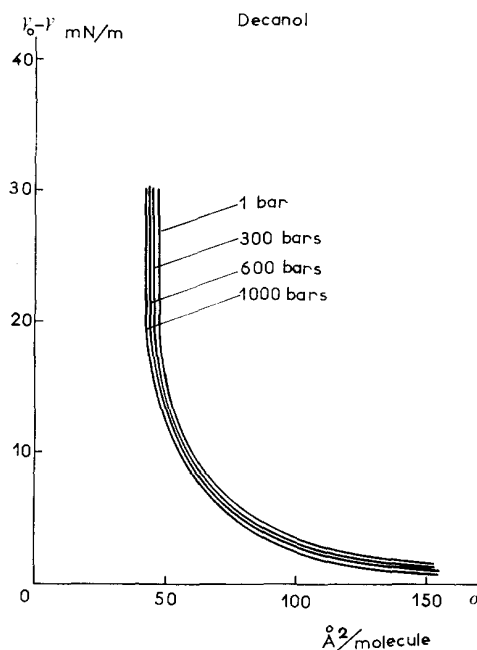


FIG. 5. Two-dimensional isotherms, interfacial pressure ($\gamma_0 - \gamma$) vs molecular area (σ) for decanol.

To describe the variation of interfacial tension with concentration, it is necessary to introduce some hypotheses about the nature of the solution in order to express in Eq. (2) the solute chemical potential. If we suppose the solution to be ideal, one may write

$$\mu_3 = \mu_3^0(T, P) + kT \ln x_3, \quad (8)$$

where $\mu_3^0(T, P)$ is the chemical potential of 3 in the pure state, at temperature T , and pressure P and x_3 the solute fraction

$$x_3 = N_3 / (N_2 + N_3).$$

The Gibbs-Duhem relation for the solution is

$$SdT - VdP + \sum_i N_i d\mu_i = 0,$$

resulting in the well known Gibbs equation⁹ valid for low concentrations

$$n_3^a = -\frac{1}{kT} \left(\frac{\partial \gamma}{\partial \ln x_3} \right)_{T, P}. \quad (9)$$

Figures 3 and 4 show the variations of γ with concentration for several values of the pressure. The slope of these curves gives the number of amphiphile molecules adsorbed at the interface. After a continuous increase, this number makes a sharp jump for a critical value x_{3c} of concentration. Plotted in Figs. 5-8 are the variations of the molecular area $\sigma = 1/n_3^a$ vs the interfacial tension difference $\gamma_0 - \gamma$ (γ_0 and γ are the interfacial tension of the pure oil and of the solution, respectively) for the four alcohols studied. To gain a better understanding of the transitions appearing on these curves, it is helpful to introduce another assumption on the nature of the interfacial solution. It will be assumed that the interfacial chemical potential of the amphiphile can be written¹⁰ in the form

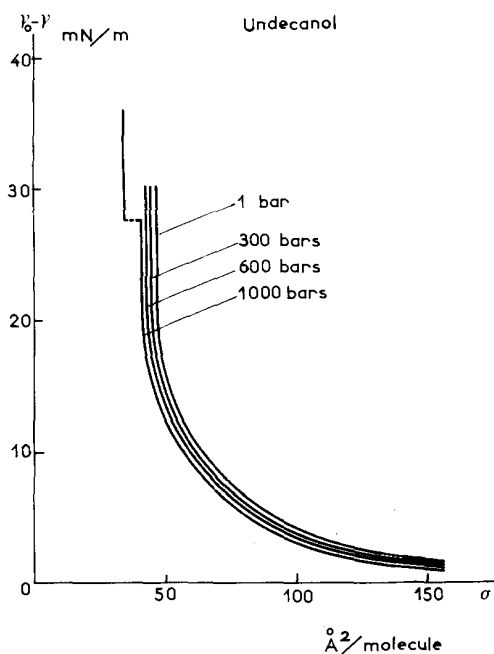


FIG. 6. Same as Fig. 5 for undecanol.

$$\mu_3^\sigma = \mu_3^{\sigma,0}(T, P) + kT \ln x_3^\sigma + w(x_2^\sigma)^2 - \gamma a_3, \quad (10)$$

where w is an interaction energy and a_3 is the area occupied by an amphiphile molecule at the interface

$$a_3 = (\partial A / \partial x_3^\sigma)_{T, P, x_2^\sigma}$$

At equilibrium, Eqs. (8) and (10) may be equated

$$\gamma a_3 + kT \ln x_3 - P \delta v_3 = \mu_3^{\sigma,0}(T) - \mu_3^0(T) + kT \ln x_3^\sigma + w(1 - x_3^\sigma)^2. \quad (11)$$

There will be a single interfacial phase so long as $\partial \mu^\sigma /$

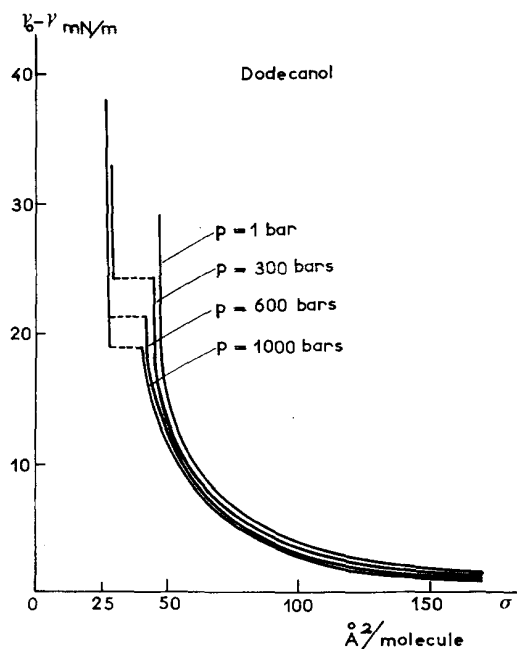


FIG. 7. Same as Fig. 5 for dodecanol.

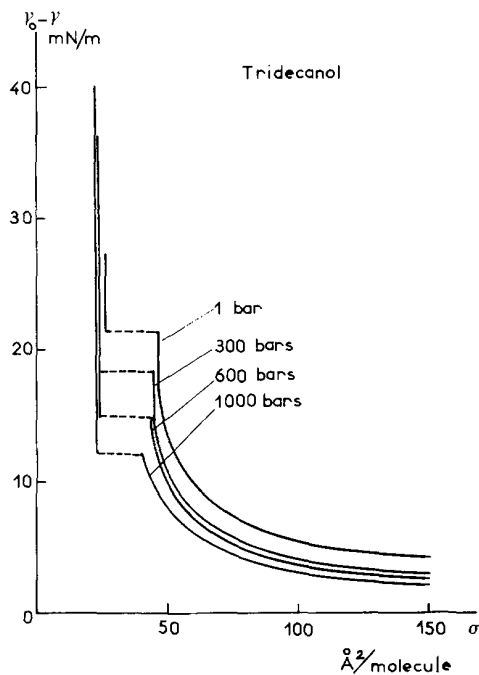


FIG. 8. Same as Fig. 5 for tridecanol.

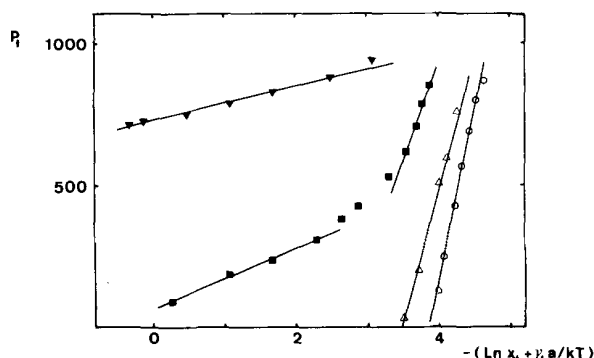
∂x_3^σ and $\partial^2 \mu^\sigma / \partial x_3^{\sigma 2}$ are positive. When the signs of these two derivatives are negative, there is a separation into two interfacial phases at equilibrium.¹¹ Accordingly, the transition occurs for

$$\begin{aligned} kT/x_3^\sigma - 2w(1 - x_3^\sigma) &= 0, \\ -kT/(x_3^\sigma)^2 + 2w &= 0. \end{aligned} \quad (12)$$

These two equalities are simultaneously satisfied whenever $x_3^\sigma = 1/2$. Inserting this value into Eq. (11) demonstrates that the transition occurs for the values γ_t and x_{3t} of interfacial tension and amphiphile concentration

$$\gamma_t a_3 + kT \ln x_{3t} - P_t \delta v_3 = \text{constant}. \quad (13)$$

On Fig. 9, this relation is plotted. There appear two sets of straight lines, one for the high concentrations (slope value at about 10^{-2}) and another one for the low concentrations (slope value at about 10^{-3}). This important change may stem from a variation of δv_3 more


 FIG. 9. Graph representing the $P_t = f(\gamma_t a_3 + kT \ln x_{3t})$ relation for (o) decanol, (Δ) undecanol, (\blacksquare) dodecanol, (\blacktriangledown) tridecanol.

likely due to an effect of the solution rather than the interface.

V. CONCLUSION

By increasing either the pressure or the concentration, it is possible to produce an increase of the number of amphiphile molecules adsorbed at the water/oil interface. For a critical value, the interfacial solution separates into two distinct phases. The condensed phase contains little or no solvent and is very similar to what is obtained with the pure amphiphile. The dilute phase is an interfacial solution where each aliphatic chain of the adsorbed molecules is solvated by the oil. The spacial structure created by the adsorption facilitates the solute-solute interaction compared to the solute-solvent interaction which is not favored by any ordered structure.

Our results can be compared only with those obtained with spread monolayers since this is the first time that a phase transition has been observed in an adsorbed layer. The monolayers spread at the air/water interface show two kinds of transition: The first one, called gas-liquid expanded (G-LE), occurs at very low density and is first order¹²; the second one, called liquid expanded-liquid condensed (LE-LC), occurs in the range 30-50 Å² per molecule and is second order.¹³ By the values of the surface density, our transition is close to the LE-LC transition, but by its order it is related to the G-LE transition. Regardless, the two systems are significantly different since in a spread monolayer there is no solvent interspersed between the chain and therefore the chain-chain interaction is of basically different nature than in an adsorbed layer and consequently comparison of the two systems cannot be carried too far.

With the lipid bilayers, a transition which is clearly first order is observed.¹⁴ Perhaps the presence of the solvent surrounding the aliphatic chains relates closely an adsorbed layer to a bilayer. Much insight may be gained on the bilayer structure by studying layers adsorbed at the oil/water interface.¹⁵

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