

Nonmonotonous Temperature Dependence of Interfacial Tensions

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Experimental data show that the interfacial tensions between water and normal alcohols present parabolic profiles as function of the temperature. In this paper, an effective microscopic model is introduced to describe these interfacial properties.

Interface properties are a subject of considerable activities from experimental, theoretical, and technological points of view. The quantity of fundamental interest in this field is the surface tension or interfacial tension τ (in the case of a liquid-liquid interface) defined as the free energy of the interface per unit of surface.

The general idea which prevails in the literature is that the surface tension is a monotonously decreasing function of the temperature T . This has been confirmed by some experiments¹ and by exact calculations.² Regarding interfacial tensions, this kind of behavior is also verified for many systems; there are, however, some remarkable exceptions like water and nicotine interfacial tension since this system presents changes in phase miscibility with temperature. Let us also point out that this temperature dependence of the interfacial tension is of crucial interest from a technical point of view, in connection with thermocapillary flows in microgravity conditions where one tries to suppress convective motions in one of the layers.³

Rather recently, new experiments were performed with water-normal alcohols of 4-12 carbon atoms.⁴ The interfacial tensions have been measured by using the Wilhelmy plate method. Looking at the results partially reproduced in Figure 1, it is easily seen that the interfacial tensions present parabolic profiles as function of the temperature.

The aim of this article is to present an effective microscopic model for such interfaces, to get a better understanding of this phenomenon. It will be shown that this model is able to reproduce the observed maxima in τ and that, using an appropriate temperature scale (related to the molecular parameters of the model), the reduced temperatures of the extrema do not seem to depend on the nature of the particular alcohol.

A few years ago, several models were considered to describe anisotropic interfaces based on random walk considerations.⁵ Due to the chemical characteristics of the molecules of alcohol (they probably are adsorbed with the carbon skeleton perpendicular to the interface; cf. Figure 2a), we expect that the interface between water and alcohol may be described by these anisotropic models.

On a microscopic scale, the interface could thus be viewed as a superposition of steps (a two-dimensional projection of these steps is given in Figure 2b.). To each step, it is tempting to associate a molecule of alcohol. This interface can thus be viewed as the delimitation curve of a set of cubes.

To describe the properties of the interface, let us introduce the height variables h_r which locate the interface with respect to some reference plane.

The energetic cost of such interface may be defined by some Hamiltonian $H(h_1 \dots h_N)$. This approach, known as an SOS type approximation, is at least correct at low temperature where the overhangs of the interface are negligible.⁶ Let J denote the fourth of the energetic cost per unit of surface, H could then be written as

$$H(h_1 \dots h_N) = J \sum_{r,r'}' a [a^2 + (h_r - h_{r'})^2]^{1/2} \quad (1)$$

where the sum \sum' is over nearest neighbors r and r' . More easily, this expression can be reduced to a Gaussian form which is exactly solvable:

$$H_G(h_1 \dots h_N) = J a^2 \sum_{r,r'}' \left(1 + \frac{1}{2a^2} (h_r - h_{r'})^2 \right) \quad (2)$$

Since this Hamiltonian characterizes the energetic cost of the interface, the surface tension τ will be given by the corresponding free energy density: ($\beta = 1/k_B T$)

$$\beta\tau = \lim_{N \rightarrow \infty} -\frac{1}{Na^2} \log Z_N(T) \quad (3)$$

where $Z_N(T)$ is the partition function associated to H_G , i.e.

$$Z_N(T) = \int_{-\infty}^{+\infty} d\left(\frac{h_1}{a}\right) \dots \int_{-\infty}^{+\infty} d\left(\frac{h_N}{a}\right) e^{-\beta H_G(h_1 \dots h_N)} \prod_{i \in \partial\Lambda} \delta\left(\frac{h_i}{a}\right) \quad (4)$$

the Dirac measures $\delta(h_i)$ simply fix all the heights of the points i which belong to the board $\partial\Lambda$ of the interface.

We thus have to compute

$$\beta\tau = \beta J + \frac{1}{2a^2} \log \frac{\beta J a^2}{2\pi} + \lim_{N \rightarrow \infty} \frac{1}{Na^2} \log \int_{-\infty}^{+\infty} dx_1 \dots \int_{-\infty}^{+\infty} dx_N e^{-\sum_{r,r'}' (x_r - x_{r'})^2} \prod_{k \in \partial\Lambda} \delta(x_k) \quad (5)$$

It remains to use the standard diagonalization procedure of Berlin and Kăc⁷ to get

$$\tau = J + \frac{1}{2a^2\beta} \log \frac{\beta J a^2}{2\pi} + \frac{1}{\beta a^2 (2\pi)^2} \int_0^{2\pi} d\omega_1 \int_0^{2\pi} d\omega_2 \log (4 - 2 \cos \omega_1 - 2 \cos \omega_2) \quad (6)$$

Computing numerically these integrals, we obtain

$$\tau = J + \frac{1}{2a^2\beta} \log \frac{\beta J a^2}{K} \quad (7)$$

where $K = 0.60981$.

For a given fixed value of a , we can compute J as a function of β from the experimental data $\tau(T)$. Simple functional relations are of the form

$$J = c\beta + d \quad (8a)$$

$$J = \frac{c}{\beta} + d \quad (8b)$$

which may be interpreted as follows: according to (8a), J may be viewed as the first two terms of a high-temperature expansion of a mean energy; according to (8b), J may be viewed as a free energy with $-c$ as an entropy like term. In both cases, once we

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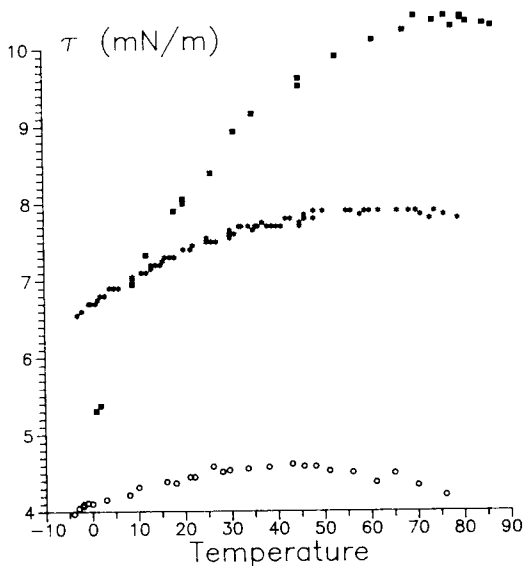


Figure 1. The interfacial tension $\tau(T)$: (O) water-1-pentanol; (*) water-1-heptanol; (■) water-1-decanol.

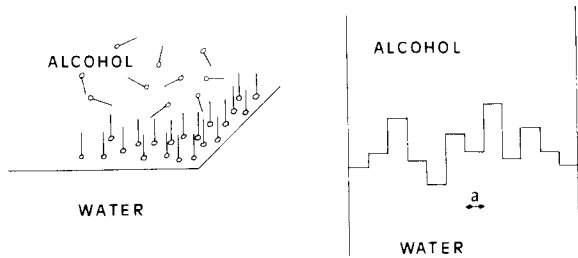


Figure 2. Sketch of the interface between water and n-alcohol: (a, left) a chemical representation; (b, right) the step model.

have the value of c and d from the best fit, we can compute the interfacial tension $\tau_{\text{theo}}(T)$ according to (7) and compare $\tau_{\text{theo}}(T)$ with $\tau(T)$ to appreciate the validity of the fits (8a) and (8b). As a function of a , the difference between $\tau_{\text{theo}}(T)$ and $\tau(T)$ may be evaluated by studying the variable

$$\Delta = \frac{1}{M} \sum_{\text{experimental points}} \frac{(\tau_{\text{theo}}(T) - \tau(T))^2}{\tau_{\text{theo}}(T)^2} \quad (9)$$

where M is the number of experimental points. One of the typical results using (8a) is represented in Figure 3 for water-heptanol. The relative error Δ with (8b) is typically 100 times bigger and does not present a sharp minimum. We therefore consider (8b) as being unable to reproduce the experimental data. All the following table and figures are thus relative to the model (8a).

For the value of a which minimizes Δ we get the results for $J(\beta)$ reproduced in Figure 4.

Similar results were also obtained for all the alcohols C_4 - C_{12} studied in ref 4. This shows, with a very good accuracy since Δ is of the order of 10^{-6} , the validity of the linear dependence of J as a function of β for all the alcohols! The corresponding results are given in Table I.

The direct consequence of the validity of this linear fit is that the energetic cost per unit of surface for this kind of interface is an increasing function of T in the considered range of temperature.

How could that be interpreted?

It should be pointed out that the model (2)-(8) only characterizes the interface with some effective interaction J . To give a microscopic derivation of τ would require treatment of a complete model of the two media. This is in fact hopeless for $d = 3$.

Some rigorous arguments may however be used to get some insight in the problem.

Let us describe the two media by a spin model, i.e., to each degree of freedom of the system A we associate a spin variable

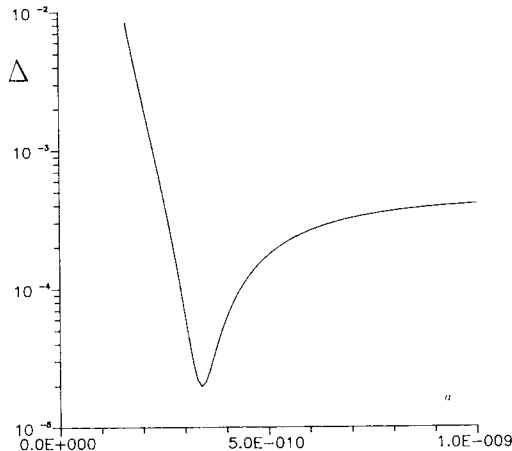


Figure 3. The relative error Δ defined in (9) as a function of the step length a for the system water-heptanol.

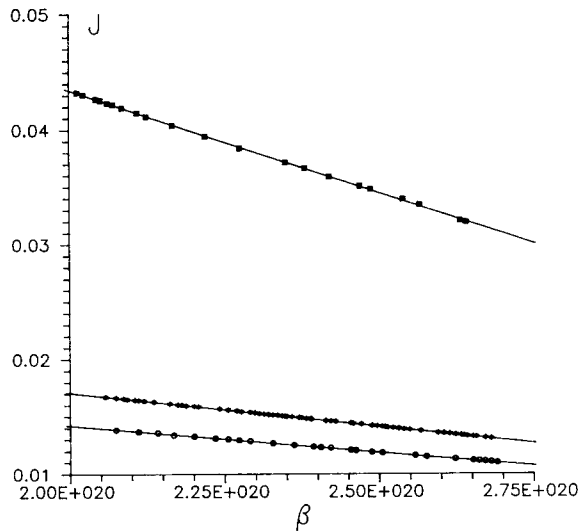


Figure 4. J as a function of β for (O) water-1-pentanol; (*) water-1-heptanol; (■) water-1-decanol.

TABLE I

	$a, \text{\AA}$	$c, \text{J}^2 \text{m}^{-2}$	$d, \text{J m}^{-2}$	T_{max}, K	T^{*a}
1-butanol	4.323	-2.813×10^{-23}	14.58×10^{-3}	293	1.764
1-pentanol	3.574	-4.648×10^{-23}	23.48×10^{-3}	314	1.779
1-hexanol	3.276	-5.792×10^{-23}	29.06×10^{-3}	322	1.783
1-heptanol	3.403	-5.844×10^{-23}	28.76×10^{-3}	334	1.772
1-octanol	3.226	-7.019×10^{-23}	33.29×10^{-3}	344	1.762
1-nonanol	2.778	-9.755×10^{-23}	44.34×10^{-3}	347	1.746
1-decanol	1.972	-1.859×10^{-22}	82.53×10^{-3}	345	1.772
1-dodecanol	2.679	-1.885×10^{-22}	79.39×10^{-3}	362	1.751

$$^a T^* = kT_{\text{max}}/a(-c)^{1/2}.$$

which takes the value +1 for some species A and -1 for the species B . The interactions between these two substances A and B may be described by some Hamiltonian

$$H = - \sum_{A \subset \Lambda} J_A \sigma^A$$

where A is a subset of Λ , J_A is a coupling constant and

$$\sigma^A = \prod_{i \in A} \sigma_i$$

It is known that, if all the couplings are ferromagnetic, i.e. $J_A \geq 0$ for all subset A of Λ , then the interfacial tension τ is monotone decreasing in the temperature T^* . Since we have here a non-monotonous surface tension, that implies that all the couplings

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J_A cannot be positive. On a physical point of view that means that we have at least two different type of interactions!

The surprising fact which comes out of our analysis is that the competition between these interactions leads to this remarkable *linear* behavior of the effective coupling constant J which is reproduced in Figure 4. The detailed microscopic description of this last property would still require some more studies.

At this stage, using a simple three-parameter model (a^2 , c , and d), we are nevertheless able to describe with a very good accuracy the behavior of the interfacial tensions between water and alcohols.

The geometric meaning of a^2 is not clear at all for the moment. It could be the cross section of a molecule of alcohol. The corresponding values of a^2 , calculated from Table I, show, however, a decreasing behavior with the length of the carbon chain which

does not support this naive geometrical interpretation.

From the value of the energetic parameter d , we deduce the order of magnitude of the energy of interaction per mole: 2 kcal/mol. This value, which corresponds to a low hydrogen bond, accounts for interactive energy between water and alcohol across the interface.

As a final remark, let us point out an intriguing property revealed by our analysis. The temperature of the maxima of $\tau(T)$ which can be determined from the experimental data (cf. ref 4) can be reduced by some energetic parameter $a^2 (-c)^{1/2}$ ($T^* = kT/a^2 (-c)^{1/2}$). It turns out that for the eight alcohols studied here (from C_4 to C_{12}) T^* of the maxima is independent of the nature of the alcohol within a few percent as can be seen in Table I.