

PART III

ADDITIONAL COMMUNICATIONS

NON-MONOTONOUS TEMPERATURE DEPENDENCE OF INTERFACIAL TENSIONS

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Let us consider two media in coexistence A and B for instance. The interface between these two media is characterized by its interfacial tension τ . As a function of the temperature T , it is generally accepted that τ should be a decreasing function. However, for some substances, τ may become a more complicated function of T . This is the case for water-(n)-alcohol of 4-12 carbon atoms media. Indeed, as shown in figure 1, τ presents a parabolic profile as a function of T within a certain range of temperature. These data have been obtained using the Wilhelmy plate method [1]

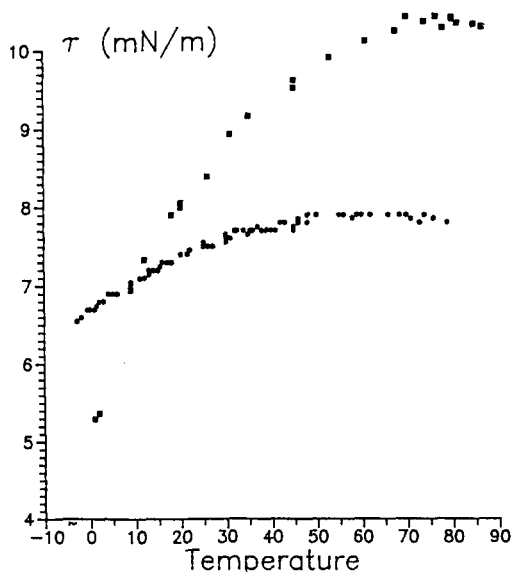


Fig. 1. The interfacial tension $\tau(T)$: (*) water-1-heptanol; ■ water-1-decanol.

In this note, we would like to introduce a microscopic model which lead to a good description of these data. More details may be found in [2].

Due to the chemical characteristics of the molecules of alcohol, it is expected that these molecules will be perpendicular to the water-alcohol interface as represented in figure 2a. This means that, on a microscopic point of view, the interface may be viewed as a superposition of steps (fig 2.b).

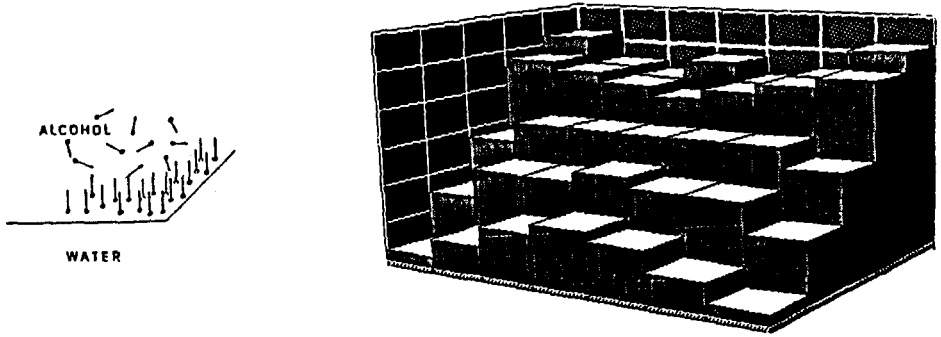


Fig. 2. Sketch of the interface between water and n-alcohol: (a) a schematic representation; (b) a step model.

Let J denote the energetic cost associated to this interface per unit of surface. The energy E_A of this interface A may thus be written as

$$E_A = J.S_A$$

where S_A represents the surface of A . To evaluate this surface, we shall introduce some variables h_i which give the height of the interface associated to the point i with respect to some reference plane (fig. 2.b).

To compute S_A as a function of $h_0 \cdots h_N$, we use some Gaussian approximation

$$S_A = \frac{J}{4} \sum_{\underline{r}, \underline{r}'} \left\{ a^2 + \frac{(h_{\underline{r}} - h_{\underline{r}'})^2}{2} \right\}$$

where a^2 is the surface of one elementary square. We therefore have the following Hamiltonian for this interface A .

$$H_A(h_{\underline{0}} \cdots h_{\underline{N}}) = -\frac{J}{4} \sum_{\underline{r}, \underline{r}'} \left\{ a^2 + \frac{(h_{\underline{r}} - h_{\underline{r}'})^2}{2} \right\}$$

The corresponding surface tension is given by

$$\tau(T) = \lim_{N \uparrow \infty} -\frac{1}{Na^2} \log \int dh_{\underline{0}} \cdots dh_{\underline{N}} e^{-\beta H_{\Lambda}(h_{\underline{0}} \cdots h_{\underline{N}})} \prod_{k \in \partial \Lambda} \delta(h_k)$$

where $\beta = 1/k_B T$ and $\partial \Lambda$ is the boarder of Λ .

After some calculations [2], we get

$$\tau(T) = J + \frac{1}{2a^2\beta} \log \frac{\beta J a^2}{0.60981}$$

This explicit result allows us to plot the experimental data in terms of J . The corresponding graph is reproduced hereafter (figure 3) and reveals surprisingly a linear behaviour of J as a function of β .

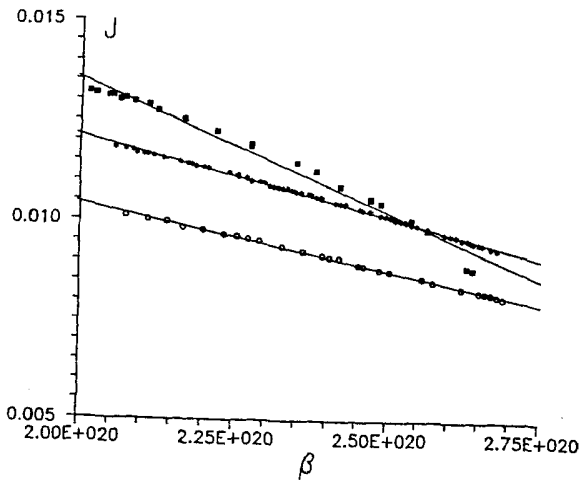


Fig. 3. The effective cost of energy J as a function of β from the experimental data given in fig. 1.

The adjusted constants of the form

$$J = c\beta + d$$

are given in the following table with the corresponding “best value” of a .

	$a(\text{\AA})$	$c(J^2 m^{-2})$	$d(J m^{-2})$	$T_{max}(^{\circ}K)$	$T^* = \frac{kT_{max}}{a\sqrt{-c}}$
n-butanol	4.323	$-2.813 \cdot 10^{-23}$	$14.58 \cdot 10^{-3}$	293	1.764
n-pentanol	3.574	$-4.648 \cdot 10^{-23}$	$23.48 \cdot 10^{-3}$	314	1.779
n-Hexanol	3.276	$-5.792 \cdot 10^{-23}$	$29.06 \cdot 10^{-3}$	322	1.783
n-Heptanol	3.403	$-5.844 \cdot 10^{-23}$	$28.76 \cdot 10^{-3}$	334	1.772
n-octanol	3.226	$-7.019 \cdot 10^{-23}$	$33.29 \cdot 10^{-3}$	344	1.762
n-nonanol	2.778	$-9.755 \cdot 10^{-23}$	$44.34 \cdot 10^{-3}$	347	1.746
n-Decanol	1.972	$-1.859 \cdot 10^{-22}$	$82.53 \cdot 10^{-3}$	345	1.772
n-Dodecanol	2.679	$-1.885 \cdot 10^{-22}$	$79.39 \cdot 10^{-3}$	362	1.751

Let us point out here that the agreement with the experimental data is less than 1% for more than 150 experimental points.

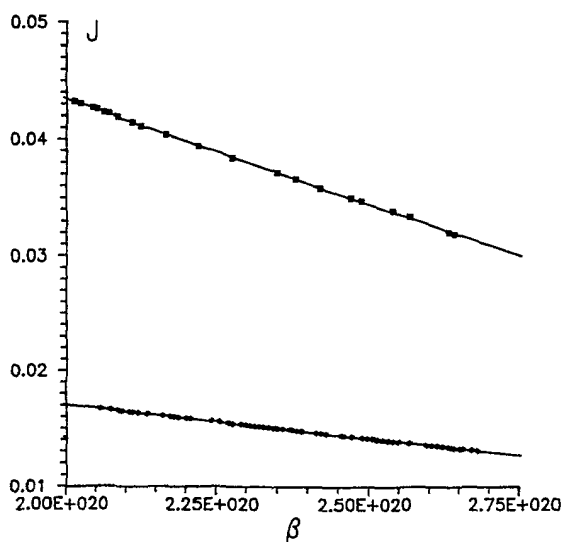


Fig. 4. The adjusted J as a function of β for (*) water-1-heptanol; (■) water-1-decanol.

Let us conclude this note by stressing the surprising linear character of J as a function of β . The origin of this property remains up to now an open question.

References

1. Villers, D. and Platten, J.; J. Phys. Chem. **92**, 4023 (1988).
2. De Coninck, J; Villers, D. and Platten, J.; J. Phys. Chem. **94**, 5057 (1990) and references therein.