Repulsion Phenomena in Thin Layers of Alcoholic Solutions of Tetrabutylammonium Iodide

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The structural disjoining pressure of methyl-, ethyl-, n-propyl, and n-butyl alcohol was determined in thin layers between highly smooth rutile surfaces when tetrabutylammonium iodide was added. The average thickness of the oriented solvation layers per interface turned out to be largest for methyl alcohol (about 1.5 nm) and decreases like the disjoining pressure when passing to the related alcohols with longer chain lengths. Tetrabutylammonium iodide clearly reduces the thickness of the boundary layer with increasing concentration.

Introduction

It is widely agreed that water adjacent to solid surfaces shows modified properties induced by an orienting effect extending from the first adsorbed and immobilized molecular layer [1 – 7]. Unfortunately, there is still a large disagreement in literature about the thickness of the boundary layer. Suffices to say that specialists in the field of electric double layers in aqueous systems have good reason to believe that immobilized aqueous layers comprise on the average only a few molecular layers in the solution phase.

Own tests with fused silica and rutile surfaces, respectively, by utilizing the disjoining pressure method [6 – 8] suggest that the mean thickness of the solvation layer, i. e. the distance over which the orienting effect has dropped to $1/e$ of its original value, in fact does not exceed this magnitude. But all evidence points to the conclusion that, provided the apparatus is sensitive enough, two surfaces still mutually feel their presence at separation distances which often exceed the order of 10 nm.

There is no question that organic liquids are likewise subject to structural change near interfaces if the polarity is large enough. This could be substantiated by disjoining pressure tests [9, 10]. Thus we should infer that primary alcohols might likewise behave in a different manner contiguous to solid surfaces.

It is the subject of this work to study the anomalous structuredness of some simple primary alcohols near very smooth rutile surfaces by the disjoining pressure method. Some further variability is introduced into the tests by addition of tetrabutylammonium iodide (Bu_4NI).

Theoretical

The interaction between two solid surfaces via an intervening liquid layer may be described by the action of four disjoining pressure components called the electrostatic (Π_{el}), the van der Waals (Π_{vw}), the adsorption (Π_a) and the structural (Π_s) component [11].

In the case of aqueous systems the operation of an electrostatic component is commonly viewed to be substantial. The formation of electric double layers on the solution side of the juxtaposed surfaces implies their mutual overlap for small gap widths which, as a result, leads to a repulsion effect. A general expression for the electrostatic disjoining pressure component, which starts from rather simple presuppositions, is given by the DLVO (Deryagin-Landau-Verwey-Overbeek)-theory [12]:

$$\Pi_{el} = 2 \cdot 10^{-3} \, c \, N_A \, k \, T \, (\cos h \, u - 1). \qquad (1)$$

c is the ion concentration in $mol \cdot dm^{-3}$, N_A Avogadro's number, k the Boltzmann constant in $J \cdot K^{-1}$ and

$$u = \frac{v \, e \, \psi_{h/2}}{k \, T}. \qquad (2)$$

$\psi_{h/2}$ is the potential midway between the surfaces, v is the ion valency. Unfortunately the weak point of the theory is that the potential ψ_0 just at the surface is not precisely known.

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The van der Waals component of the disjoining pressure in the interlayer was found to be attractive according to [13, 14]

$$\Pi_{vw} = - A / 6 \pi h^3 \qquad (3)$$

if the separation distance does not exceed the order of 200 nm, where retardation effects come into play. h is the thickness of the interlayer and A the composed Hamaker constant of the system solid/liquid/solid. To be exact, the intervening aqueous layer is according to our view non-uniform in its structure and should, therefore, exhibit an individual Hamaker constant varying with the distance reckoned from one of the surfaces [14]. For the sake of clearness we will neglect this minor effect in our further considerations.

Additional problems are encountered if, for instance, binary solutions are considered. Neutral molecules, particularly if they can strongly interact with the solid surface, will form an adsorption layer which is usually multimolecular in its nature obeying a Boltzmann distribution. For sufficiently small surface separations the more diffuse parts of the adsorption layers will interpenetrate and cause a repulsive adsorption component of the disjoining pressure [11].

The underlying theory including the adsorption as well as the van der Waals component was given by Deryagin et al. [15] and yields the total quantity

$$\Pi_t' = \frac{k T \chi_{1\infty}}{v} \frac{\partial}{\partial h} \left\{ \int_{\delta}^{h-\delta} [f(h \cdot x) - 1] dx \right\} - \frac{A}{6 \pi h^3} . \qquad (4)$$

$\chi_{1\infty}$ is the mole fraction of the solute (substance 1) in the bulk solution in which the interfacial system is imbedded, v the molecular volume of the solvent (substance 4), δ the thickness of the first adsorbed monolayer, x a distance coordinate reckoned from one of the two surfaces into the interior of the interlayer, and A the Hamaker constant of the system [13] referring to the pure solvent.

The first term in the integral expression of (4) is defined by

$$f(h \cdot x) = \frac{\chi_1(x)}{\chi_{1\infty}} = \exp \left[\frac{A_2}{k T} \left(\frac{1}{x^3} + \frac{1}{(h-x)^3} \right) \right], \qquad (5)$$

when the interlayer is sandwiched between two solid phases (2 and 3), which in the present case are regarded to be exactly equal. $\chi_1(x)$ describes the distance dependence of the mole fraction of the

solute across the interlayer. The constant A_2 is given by

$$A_2 = \frac{\hbar}{16 \pi^2} \int_0^\infty \left(\frac{\varepsilon_2 - \varepsilon_4}{\varepsilon_2 + \varepsilon_4} \right) \cdot \left(\frac{\partial \varepsilon_{14}}{\partial N_1} \right)_{N_1 = 0} \cdot \frac{d\omega}{\varepsilon_4} . \qquad (6)$$

The dielectric permittivities $\varepsilon = \varepsilon(i \omega)$ are functions of the angular frequency ω. The subscript refer to the phases quoted above. ε_{14} is the dielectric permittivity of a solution of substance 1 in the solvent 4. The concentration of the former is N_1 molecules per unit volume of the solution.

The structural part of the disjoining pressure Π_s is still poorly understood, particularly for the case that substances dissolved in the liquid interlayer phase have a pronounced influence on the formation of multimolecular solvation layers at interfaces.

Adlfinger and Peschel [16] introduced for the dependence of Π_s on the interlayer thickness the empirical expression

$$\Pi_s = C_s e^{-n_s h} \qquad (7)$$

with C_s and n_s as parameters which can be derived from experiment. The corresponding structural disjoining force may be written in the simplified form

$$dF_s = \frac{2 \pi e^{-n_s / r_f}}{n_s^2 f^2} C_s e^{-n_s h} \qquad (8)$$

if the contact is brought about by a spherical and a planar surface and the real surface roughness is taken account of (parameters f and r_f [6, 16]).

For the case of a high-grade politure it is tempting to regard the two juxtaposed real surfaces as ideally smooth. The disjoining pressure in the planar/spherical system is then given by

$$dF_s = \frac{2 \pi R}{n_s} C_s e^{-n_s h} \qquad (9)$$

as pointed out in a recent paper [17]. R is the curvature radius of the spherically formed solid surface.

Some degree of refinement is achieved if h is replaced by $h' = h + 2 R_b$, where R_b is the average depth of the surface roughness obtained by mechanical or interferometric methods, respectively.

Since there is still much controversy about the extent of structuring of liquid near interfaces our considerations in the following should be focused on this subject.

One problem inherent in the estimation of surface zone structuring is the free excess energy $(\Delta F^E)_{2\delta}$ needed to extrude the more or less oriented liquid from the space between the surfaces by approaching them down to a distance of $h = 2\,\delta$, where only the first adsorbed layers on both the surfaces will be left. Their free energy is chiefly determined by the interfacial energy γ in the solid/liquid system.

Accordingly we can write for the free excess energy

$$(\Delta F^E)_{2\delta} = -\int\limits_{\infty}^{2\,\delta} \Pi_s(h)\,\mathrm{d}h\,. \tag{10}$$

This quantity should contribute to only a small extent to the free interfacial energy, otherwise the validity of the Bet multimolecular adsorption theory would be invalidated. Hence, we had to expect

$$(\Delta F^E)_{2\delta} \ll 2\,\gamma\,. \tag{11}$$

Experimental

The experimental device and the procedure of the disjoining pressure tests developed by us are described in former papers [6, 16]. The essential process during a run is the very slow (quasi-static) approach of a planar and a spherically formed plate both being placed in the liquid phase questioned. The plates (radius $7 \cdot 10^{-3}$ m and thickness $7 \cdot 10^{-3}$ m) were cut from a single crystal of rutile in the (001) plane and polished to a very high surface quality ($R_b = 2.5$ nm). In the course of preliminary tests with water the rutile surfaces got most probably fully hydroxylated. The existence of hydroxyl groups on rutile surfaces is well established by infrared spectroscopy [18 – 21]. From the geometry of the rutile surface asperities we derived $f = 1.5 \cdot 10^{-4}$ and $r_f = -8 \cdot 10^{-3}$ nm [16].

It must be emphasized that before each test the measuring cell and the plates were carefully degreased and then kept extremely dry.

Tetrabutylammonium iodide, methanol, ethanol, propanol-1, and butanol-1, provided by Merck, Darmstadt, were of analytical grade. The alcohols were dried by using a column filled with a molecular sieve (G. T. Baker; 1509, 0.3 nm); before use they were fractionally distilled. Preliminary tests referring to the adsorption of tetrabutylammonium iodide on the interior walls of the measuring cell did not reveal any quantitative effect beyond the limits of error.

Results

From the disjoining pressure studies we derived the parameters n_s and C_s in (7) by carrying out numerous sets of measurements with different alcoholic solutions of tetrabutylammonium iodide. The electrolyte concentration ranged between 10^{-7} and 10^{-3} mol dm^{-3}; the solvents used were methanol, ethanol, propanol-1, and butanol-1.

Let us first focus on the disjoining pressure results of the pure alcohols in thin layers between rutile plates. Figure 1 displays the n_s^{-1} values for the pure compounds on the left side of the subdivided diagram. It is clearly evident that the average thickness of the immobilized boundary layer decreases when passing from methanol to butanol-1. To be sure, the thickness values refer to ordered layers sandwiched between *two* solid surfaces. With respect to *one* surface we have to take half the values which correspond to about $2 - 4$ molecular layers which were likewise found in the case of water near rutile surfaces [8, 22].
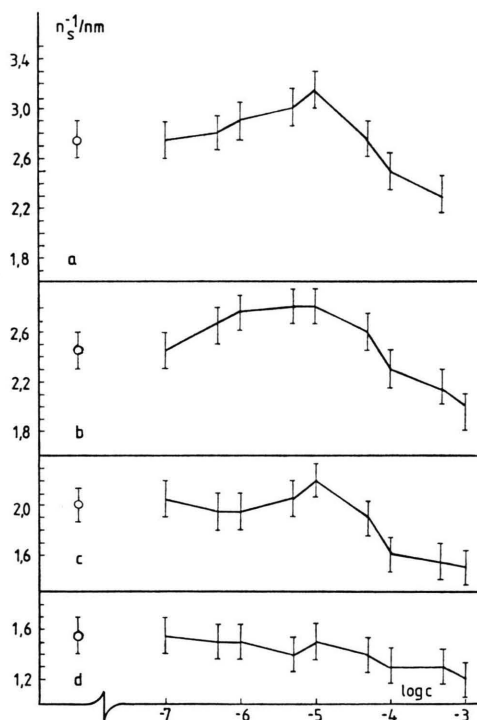

Fig. 1. The average thickness n_s^{-1} of the immobilized boundary layer of different alcoholic solutions of tetrabutylammonium iodide between two rutile plates. Solvents: a) methanol, b) ethanol, c) propanol-1, d) butanol-1. The data on the left refer to the pure compounds. $T = 293$ K (c in mol dm^{-3}).

The method, however, imposes severe limits to the exact determination of the n_s^{-1} values since they display the order of the roughness of the two opposing plate surfaces. This would in the first instance suggest that the n_s^{-1} values were for the most part created by some sort of mutual gearing of the surface asperities. But this could be ruled out, since disjoining pressure tests under similar conditions with carbon tetrachloride, which is not expected to display any multimolecular adsorption effects lead to values $n_s^{-1} < 0.5$ nm just below the limit of detection [23]. All these findings are certainly not without interpretative difficulty. In order to allow for not too large errors the n_s^{-1} values were always determined for not too close separations where no implications by surface asperity contacts might be anticipated. The error bars refer to relative tolerances only.

A significant question concerns the influence of traces of water dissolved in alcohol on the n_s^{-1} values. We have studied in a number of experiments the splitting behavior of thin layers of alcohol/water mixtures between fused silica surfaces [24]. Starting from pure alcoholic fluids, addition of water up to a concentration of 1 mol dm^{-3} lowered the n_s^{-1}-values by about 10%. Hence there is no question that traces of water which might enter the alcoholic phase during filling up the measuring cell do not affect the average solvation layer thickness of the pure compound to any notable extent.

The behavior of the structural part of the disjoining pressure is by far more difficult to outline because Π_s can according to (8) and (9) be obtained by two different procedures. Let (8) refer to method I and (9) to method II in evaluating the disjoining pressure values. In Fig. 2 the results for all four alcoholic fluids and solutions of butylammonium iodide, respectively, in thin layers are represented according to method I for two plate separations. Figure 3 illustrates analogous results according to method II. Repulsion effects for plate separations $h = 10$ nm clearly lay out of the range of detection of our apparatus; but since we assume knowledge of the values of C_s and n_s it is quite easy to compute the corresponding disjoining pressure quantities.

The disjoining pressure values similar to those of n_s^{-1} decrease in the order

methanol $>$ ethanol $>$ propanol-1 $>$ butanol-1 .

Evidence suggests that the electrolyte added apparently breaks the structure of the solvation layer with increasing concentration as is required by theory.

We think it is instructive to briefly consider the magnitude of the free excess energy of the modified boundary layer according to (10). As an example we chose methanol and methanolic solutions of Bu$_4$NI since they exhibit the largest effects. By putting $\delta = 0.5$ nm we obtained results which are portrayed in Figure 4.

Discussion

Let our attention first be directed to the different depths of the ordered boundary layers of the primary alcohols tested. The question why just methanol shows the largest surface structuring cannot be answered in a straightforward manner. As pointed out in the foregoing the surface roughness primarily affects the n_s^{-1} values, which is a serious obstacle in presenting accurate data. Further the complex structure of the bulk liquid alcohol phase makes it difficult to provide a rationale for the different interfacial properties.

According to some former experimental evidence [9, 10] pure alcoholic fluids should produce more extended solvation layers when displaying a less associated structure. Analogous cases are known from water and aqueous electrolyte solutions [6, 7]. There is no question that the order is particularly induced by the surface hydroxyl groups via hydrogen bonding with the alcohol molecules nearby, which are moreover exposed to the rather strong crystal field of rutile producing polarization effects [25]. These surely support molecular immobilization.

The involvement of highly associated species (tetramers and highly n-mers) in the structural arrangement of primary alcohols or hydrocarbon-alcohol mixtures has often been stressed in literature [26 – 35]. It is generally assumed that tetramers and pentamers (especially cyclic ones) exist in the bulk phase up to a high percentage.

Bartczak [36] has elaborated a theoretical model which is concerned with the hydrogen-bonded molecular structure of alcohols. In a somewhat sophisticated picture he assumes the hydrogen bond energy for simple primary alcohols to have the value $\Delta H_b = -21.34$ kJ mol^{-1}. In context with the

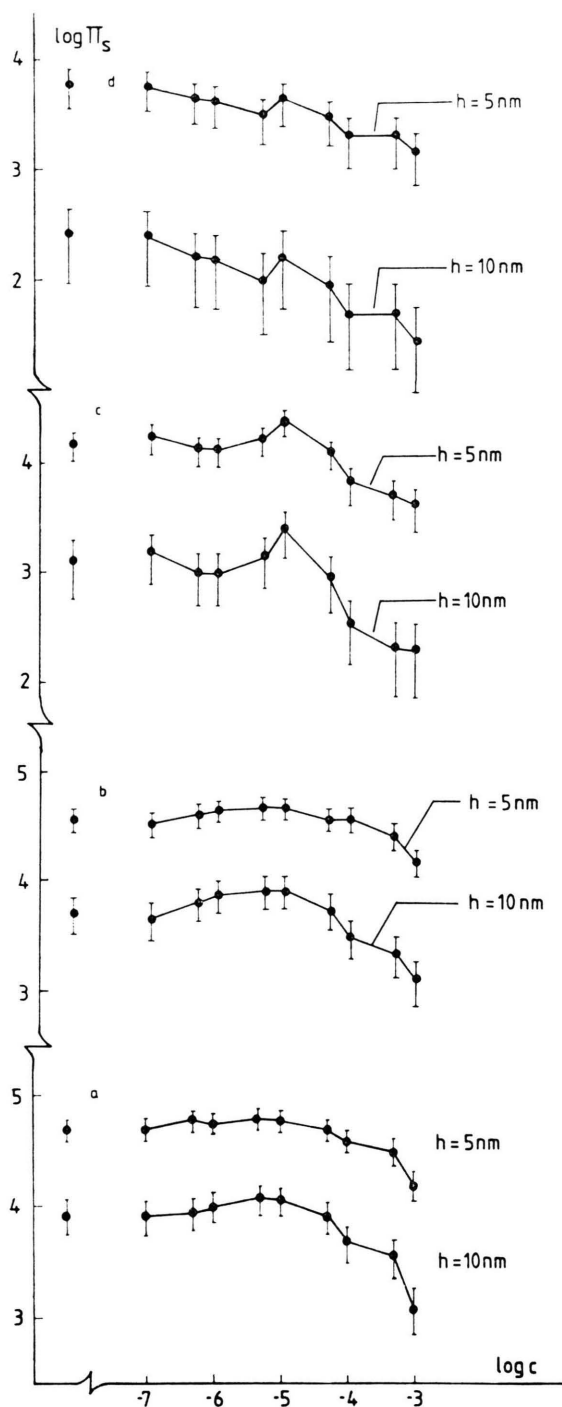Fig. 2. Double-logarithmic plot of the structural disjoining pressure* against the concentration (in mol dm⁻³) of tetra-butylammonium iodide dissolved in a) methanol, b) ethanol, c) propanol-1, d) butanol-1 for two different plate separation distances according to method I. The data on the left refer to the pure alcoholic compounds. $T = 293$ K.
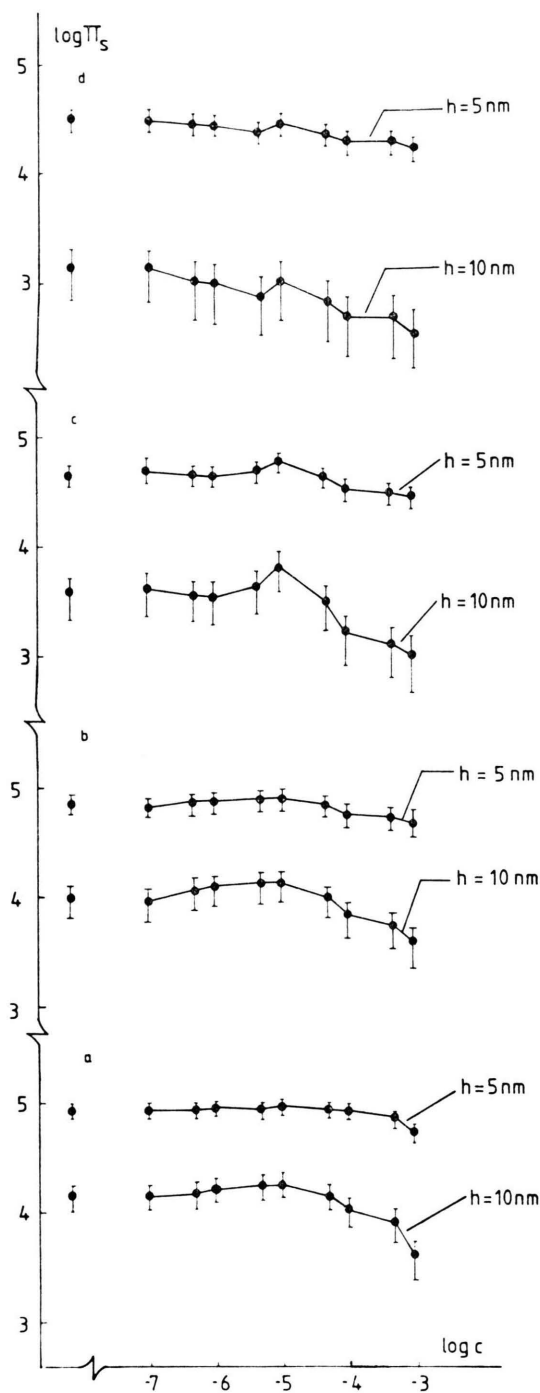
Fig. 3. Double-logarithmic plot of the structural disjoining pressure* against the concentration (in mol dm⁻³) of tetra-butylammonium iodide dissolved in a) methanol, b) ethanol, c) propanol-1, d) butanol-1 for two different plate separation distances according to method II. The data on the left refer to the pure alcoholic compounds. $T = 293$ K.
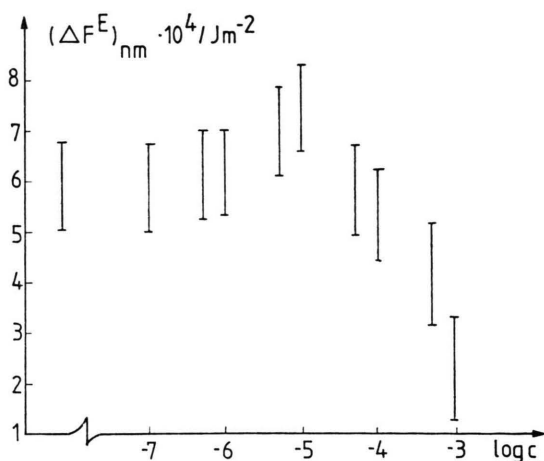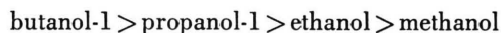
* in N/m².

Fig. 4. Free excess energy of the intervening layer ($2\delta =$ 1 nm) consisting of a dilute aqueous solution of methanol (c in mol dm^{-3}).

present problem it is of interest that the self-association of the alcohols was found in the order

butanol-1 > propanol-1 > ethanol > methanol

in agreement with findings by Fletcher [31]. It is true, however, that Luck [37] by tests in the infrared overtone region found that the content of free hydroxyl groups in liquid methanol and ethanol is about the same. On the other hand, the differences in the free energies of the immobilized boundary layers beyond the first adsorbed molecular layer according to (10) (detailed data see below) is so small that the results obtained by Luck should be irrelevant to a discussion of our findings.

In principle, Π_t' as defined by (4) actually participates in the overall splitting effect. It is only the question if Π_t', by varying the Be$_4$NI concentration, reaches values which are worth mentioning. At the present time the validity of (4) has been hardly checked. Deryagin et al. [15], however, have carried out some calculations relevant to our problem. For a related case they propose to put $A = 10^{-21}$ J, and $A_2 = 10^{-50}$ Jm^3; they present plots of Π_t' for different $\chi_{1\infty}$ values (0, 0.01, 0.05, and 0.1) (Figure 4).

In our tests the molar fraction of Bu$_4$NI in the bulk was at most $\chi_{1\infty} = 3.2 \cdot 10^{-5}$. That part of the electrolyte which is dissociated in the alcoholic solvent contributes chiefly to the electrostatic portion of the overall disjoining pressure.

Evans and Gardam [38] have determined association constants for Bu$_4$NI in ethanol and propanol-1 by conductance measurements. They report values of 123 ± 3 and 415 ± 6, respectively. For the highest concentration used (10^{-3} mol dm^{-3}) simple calculations tell us that Bu$_4$NI is associated in ethanol to about 10%, in propanol-1 to about 24%. For lower concentrations the association gets smaller.

The results illustrate that for 10^{-3} mol dm^{-3} the concentration of the associated portion is about $2.4 \cdot 10^{-4}$ mol dm^{-3} or lower. This situation applies well to graph 1 in Fig. 5 which according to Deryagin et al. [15] describes the distance dependence of Π_t' for $\chi_{1\infty} = 0$. It is evident that for high dilutions the adsorption component of the disjoining pressure can be discarded. The attractive component, which is apparently masked by the stronger repulsive one, could not yet be detected by our method with sufficient accuracy.
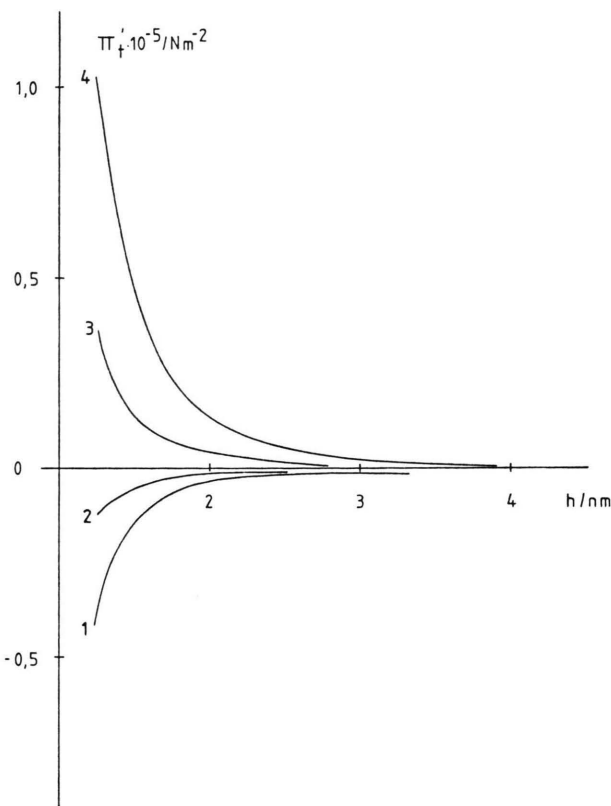

Fig. 5. Isotherms of Π_t' in liquid interlayer of a binary solution between two dielectric plates for different molar fractions of the solute.
($\chi_{1\infty} = 0$ (1), 0.01 (2), 0.05 (3), and 0.1 (4)) (after Deryagin et al. [15], with permission).

The graph in Fig. 4, which is based on (10) for $2\,\delta = 1$ nm, proves that the free excess energy of the surface zone beyond the first adsorbed molecular layer is negligibly small when being compared with the ordinary interfacial free energy, which in the present case and regarding one surface only, might have the order of about 0.2 J m^{-2}. Just this underlines the strong validity of the relation (11), which is assumed to be a prerequisite for the discussion of structural anomalies in surface zones.

Regarding pure methanol and ethanol we have found for $(\varDelta F^{\mathrm{E}})_{1\,\mathrm{nm}}$ on the average about $6.0\cdot10^{-4}$ J m^{-2} and $4.5\cdot10^{-4}$ J m^{-2} respectively. The difference amounts to about $1.5\cdot10^{-4}$ J m^{-2}, i. e. methanol and ethanol differ in their free surface excess energies by only a very small amount, though this quantitative test is still rather provisional.

Unfortunately our technique did not give any experimental evidence for the existence of the electrostatic part of the disjoining effect in alcoholic electrolyte solution layers. This could be due to insufficient sensitivity of the device. It is clear, however, that under these peculiar conditions the electrostatic repulsion can only reach minor values.

The conclusion is that primary alcohols in wetting contact with a solid surface are capable of creating a multimolecular solvation layer. The precise calculation of the corresponding structural disjoining pressure, however, leaves much to be desired, because of the remaining surface roughness of the plates used. Thus, two different methods of evaluation were utilized which both show serious drawbacks.

Acknowledgement

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