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Surface forces in thin liquid films of *n*-alcohols and of water–ethanol mixtures confined between hydrophobic surfaces

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ABSTRACT

An atomic force microscope (AFM) was used to measure the surface forces in thin liquid films (TLFs) confined between gold surfaces hydrophobized by chemisorption of alkylthiols. The measurements were conducted in different H-bonding liquids and in water–ethanol solutions. Attractive forces stronger and longer-ranged than the van der Waals force were observed in water, ethanol, and 1-butanol in a descending order. The attractive force measured in methanol was much weaker.

The surface forces measured in ethanol solutions varied with concentration. Initially, the attractive forces decreased rapidly upon ethanol addition, passed through a broad minimum centered around mole fractions in the range of 0.15–0.20, and then increased as the ethanol mole fraction was further increased above ~0.5. Thermodynamic analysis of the data suggests that clusters of water and ethanol may form in TLFs. Thus, the attractive forces may arise from changes in liquid structure. It appears that structuring is a consequence of H-bonding liquid to minimize its free energy in the vicinity of hydrophobic surfaces and in the presence of foreign species in solution.

1. Introduction

Thin liquid films (TLFs) of water or an aqueous solution confined between two surfaces control the stability of colloids, foams, wetting films, adhesive joints, *etc.* The DLVO theory has been used successfully to predict the stability by balancing two surface forces, i.e., the van der Waals and electrical double-layer forces, present in the films. It has been suggested, however, that the theory is applicable only for surfaces whose water contact angles (θ) are in the range of 20° and 40° [1]. Outside this range, other types of forces may also play a role.

The wetting films formed on *hydrophilic* surfaces (e.g., quartz and mica) are thicker than predicted due to the presence of hydration force [2,3], while those formed on strongly *hydrophobic* surfaces are less stable than predicted due to the presence of hydrophobic force. As a consequence, the DLVO theory cannot predict the bubble–particle interactions in flotation, in which minerals are selectively hydrophobized to destabilize wetting films. It has been shown that the rate of film thinning increases with increasing hydrophobicity (or contact angle) of the minerals to be floated [4,5]. These difficulties point to the problem that the continuum (mean field) approximation used in deriving the DLVO theory may be applicable only for surfaces within the narrow range of contact angles noted above.

It has been shown that the water adlayers formed on hydrophilic mica surfaces grow epitaxially [6], which may explain the difficulties in modeling water adsorption isotherms based on continuum theories [7]. Also, a recent molecular dynamic (MD) simulation showed that water confined between hydrophobic graphite slabs forms well-ordered structures with their dipoles oriented parallel to the graphite surfaces [8]. Further, water freezes under ambient conditions in carbon nanotubes [9]. It appears, therefore, that water in the vicinity of a surface can have a structure that is distinct from that of bulk water but that is determined in part by the atomic constitution of the substrate.

We recently measured the surface forces in TLFs of water confined between hydrophobic surfaces at several different temperatures to derive more complete thermodynamic information than was previously available [10]. The measurements were conducted using gold surfaces hydrophobized with *n*-alkylthiols (C_nSH) with $n = 2$ and 16 by means of an atomic force microscope (AFM). It was found that the long-range hydrophobic attractions become stronger with decreasing temperatures, and that both the excess film entropy per unit area (S^f) and the corresponding enthalpy (H^f) decrease with decreasing film thickness. The decrease in enthalpy may be due to enhanced formation of H-bonded clusters of water, while the decrease in entropy change multiplied by temperature ($T\Delta S^f$) represents a net thermodynamic cost for forming

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clusters and subsequently mixing them with the rest of the water in the thin film.

The H-bonded clusters we refer to here may be related to the low-density liquid (LDL) species that are known to be present in bulk water even at ambient conditions [11,12]. The LDLs may be more readily formed in the TLFs confined between hydrophobic surfaces than in the bulk as the water molecules that are not H-bonded to the surfaces are in higher free energy states. It was concluded, therefore, that hydrophobic forces originate from structural changes associated with film thinning [10], as suggested originally by Rabinovich and Derjaguin [13] and elaborated in detail by Eriksson et al. [14,15].

In the present work, we further explored the notion that hydrophobic force may be of structural origin. To this end, AFM force measurements were conducted using gold surfaces hydrophobized with n-alkylthiols (C_nSH) of $n = 4$, 12 and 16 in different H-bonding liquids. A solid is hydrophobic when the work of cohesion of water (W_c) is larger than the work of adhesion (W_a), the major component of which is H-bond energy for hydrophilic surfaces. One can control the hydrophobicity and hence hydrophobic force by control of W_a using surfactant. It should also be possible to control the hydrophobicity and hydrophobic force by control of W_c. In the present work, we conducted the force measurements in different H-bonding liquids (methanol, ethanol, 1-butanol, and water) and in water–ethanol mixtures as a means to control W_c – a liquid property.

It has been well documented that the structure of ethanol–water mixtures is a complex function of concentration. In principle, mixing of two liquids should entail an increase in entropy. When ethanol is admixed into water, however, the entropy increase is far less than anticipated [16,17], reaching a minimum at a mole fraction (x_2) of approximately 0.2, while the enthalpy becomes lower than anticipated [18,19]. These findings suggest that some type of structure is forming when alcohol and water are intermixed. An earlier explanation was hydrophobic hydration or 'iceberg' formation [20], implying that low-entropy cages are formed with relatively strong H-bonds in the first hydration shell of the apolar moiety of an alcohol molecule. More recent molecular dynamic and neutron diffraction studies showed, however, that the low entropy is due to incomplete mixing at the molecular level rather than hydrophobic hydration. It has been shown also that in the presence of ethanol, water–water correlation is enhanced, promoting local water structure [21]. Further, the size of the clusters increase with increasing ethanol concentration [22].

As the surface tension of ethanol is 22.22 $\mathrm{mN\,m^{-1}}$ and that of water is 71.94 $\mathrm{mN\,m^{-1}}$ at 25° [23], the former should adsorb at the air/water (or hydrocarbon/water) interface. Butler and Wightman [24] showed that the Gibbs surface excess quantity reaches a maximum of $\Gamma_{2(1)} = 4.3 \times 10^{18}$ molecules per m^2 at $x_2 \approx 0.17$. More recently, Aratono et al. [25] reported an extended set of surface tension data for water (1)–ethanol (2) mixtures that are in full agreement with those obtained by Butler and Wightman and by Teitelbaum et al. [26]. These results have recently been verified by the sum-frequency vibrational spectroscopy (SFVS) studies showing that the signal from the terminal methyl (CH_3) groups of ethanol increases rapidly with concentration, reaching a maximum at $x_2 = 0.2$ [27] and subsequently decreasing at higher concentration. It was shown also that the 3700 $\mathrm{cm^{-1}}$ peak characteristic of the dangling OH-groups at the octyltrichlorosilane (OTS)-coated silica and methanol solution interface decreases with increasing alcohol concentration, reaching a minimum $x_2 = 0.2$. Further, the solubility of oxygen (O_2) in ethanol solutions reaches a minimum at the same mole fraction [28]. Apparently, the structure of alcohol solutions undergoes a transition at $x_2 \approx 0.2$.

In the present work, the surface force data obtained in ethanol solutions were analyzed using the Derjaguin approximation [29] to determine the changes in film tension ($\Delta\gamma^f$) in the same manner as described previously [10,14]. The film tension data were then used to determine the changes in excess ethanol ($\Delta\Gamma_2^{f,\mathrm{ex}}$) in TLFs using the thin film analogue of the standard Gibbs adsorption equation. The results showed that the excess quantities are negative at x_2 below ~0.2 and become positive above this value, suggesting that the long-range attractions observed in ethanol solutions may be related to structural changes of the liquid core of the TLFs.

2. Experimental

2.1. Materials

A Nanopure III (Barnstead) water purification system was used to obtain double-distilled, deionized water with a resistivity of 18.2 MΩ·cm at room temperature. To remove particulates, a Post-filter (0.2 μm in pore size, Fisher Scientific) was integrated with the purification system. 1-butanethiol (C_4SH, 97%), 1-dodecanethiol ($C_{12}SH$, >95%) and 1-hexadecanethiol ($C_{16}SH$, ⩾97%) were obtained from TCI America and used to hydrophobize the gold substrates. Ethanol (200 proof) was obtained from Aaper Alcohol, methanol (99.8%) from Fluka, and 1-butanol (HPLC) from Fisher Scientific. The gold substrates were cleaned with H_2SO_4 (98%, VMR International) and H_2O_2 (29.0–32.0%, Alfa Aesar). All reagents were used as received.

Gold-coated glass slides were obtained by depositing pure gold onto glass using a vacuum evaporator. A 50 Å chromium layer was deposited first, followed by a layer of gold with a thickness of 500 Å. The chromium layer was needed to ensure a strong adhesion of gold on the surface. Gold spheres of various diameters were produced as described by Raiteri et al. [30]. In this procedure, a gold wire (0.0127 mm diameter, 99.9%, Alfa Aesar) was short-circuited at 120 V AC to create a cloud of gold particles, which were collected over a petri dish. Only the spheres of 10–20 μm diameters were selected for force measurements. For each experiment, a gold sphere was glued onto the tip of an AFM cantilever with EPON 1004 resin (Shell Chemical Co.) under a microscopic field using a homemade micro-manipulator.

2.2. Preparation of hydrophobic surfaces

To obtain high-quality self-assembled monolayers of thiols, it is necessary to clean gold substrates thoroughly [31,32]. There are several cleaning procedures available for gold substrates, which include the methods of using "piranha" solution (1:2 H_2O_2/H_2SO_4 by volume) [33,34], chromic acid [35,36], and UV/ozone treatment [31,37]. In the present work, flat gold plates were cleaned first by immersing them into a boiling piranha solution for 20 min. The plates were then flushed with pure water for 1 min to remove the residual piranha solution, rinsed with pure ethanol for 2 min, and then washed thoroughly with ethanol. The AFM images of the clean gold surfaces showed a root-mean-square (RMS) roughness of 0.8 nm over an area of 1 × 1 μm^2.

The gold surface cleaned in the manner described above exhibited zero water contact angle (θ), most probably due to the presence of gold oxides (Au_2O_3) formed in the piranha solution [38]. However, the oxidation product is thermodynamically unstable and can be readily decomposed by ethanol [30,31]. Cleaning the plate with ethanol increased the water contact angle to 65°.

The gold spheres, on the other hand, could not be cleaned using the piranha solution, as they were glued onto AFM cantilevers. The sphere-cantilever assembly was washed first with pure ethanol, irradiated by UV light (254 nm) for 2 h, and then rinsed with ethanol again.