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Colloids and Surfaces A: Physicochemical and Engineering Aspects

Atypical wetting behaviour of alcohol–water mixtures on hydrophobic surfaces

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HIGHLIGHTS

- Aqueous solutions of alcohols exhibit certain specific properties, such as viscosity maximum or high contact angles.
- These phenomena are caused by a complex inner structure of alcohol–water mixtures.
- The existence of small aggregates consisting of water and alcohol molecules is assumed both in bulk liquid and on interface layers.
- Aggregates are stable over time and influence the surface tension and wettability.

GRAPHICAL ABSTRACT
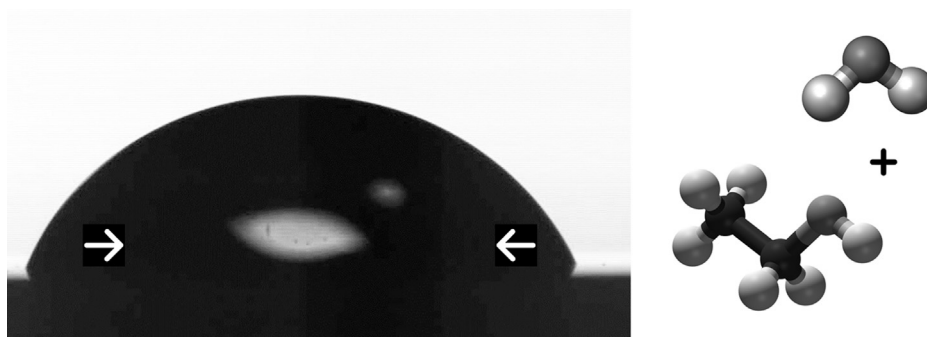
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ABSTRACT

Methanol, ethanol, n-propanol and their aqueous solutions are widely used in many industrial applications where wettability is one of the most important parameters. This project was focused on the experimental study of the wetting behaviour of these mixtures on two similar hydrophobic surfaces in the full concentration range. Based on the measurements of dynamic surface tension and dynamic liquid drop spreading we proved the stable composition of liquid layers on the solid–liquid and liquid–air interfaces. Likewise, in bulk liquid the existence of small aggregates consisting of water and alcohol molecules is assumed. This complex internal structure of aqueous solutions of short chain alcohols influences the surface properties of these solutions and explains the higher contact angles when compared to pure liquids with similar surface tension.

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1. Introduction

Alcohols, along with surface active agents (surfactants), are used in many industrial applications. Flotation of plastics is a good example. Here, waste plastic materials are separated according to their wettability and/or liquid surface tension. At appropriate values of liquid surface tension, air bubbles adhere onto the particles with lower wettability, promoting flotation, whereas particles having higher wettability will be wetted sufficiently without bubble attachment. An appropriate substance which is commonly used to control the surface tension of flotation liquids is an aqueous solution of a simple alcohol, such as methanol or propanol [1]. Due to the development of new materials and their surfaces, the surface wettability or nonwettability is a very important material property. New materials are developed as hydrophobic, but a small addition of alcohol or surfactant could change this hydrophobicity

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into hydrophilicity. Water–alcohol mixtures are also widely used and studied due to their important role in biological systems, and pharmaceutical and technical applications. In these applications, alcohols are used both in low concentrations (as co-surfactants) as well as in high concentrations (co-solvents). The systems consisting of alcohols and surfactants are studied with emphasis on adhesion mechanism [2–6], evaporation [7,8], micellar structure and dynamics, etc. Together with this research, experimental studies of the internal structure of aqueous alcohol mixtures are also being carried out. Hydrogen bonding liquids, such as alcohols, have a rich microstructure that the stronger hydrogen bonding water does not seem to possess. It was found that simple alcohols are micro heterogeneous since they tend to develop distinct local microstructures, which are dependent on the geometry of the constitutive molecules such as chainlike structures or micelle like structures. The polarity of water and alcohol self-association as well as cross-association between water and alcohol show significant impacts on physical and chemical properties, like the existence of a viscosity-composition maximum, decrease of partial molar volume or interfacial properties [3,9].

The objective of this paper is to present some new results on the wetting behaviour of alcohol solutions. The project is focused on the experimental study of wetting properties of aqueous solutions of short chain alcohols (methanol, ethanol and *n*-propanol in full concentration range) on two hydrophobic surfaces with similar surface energy. The mutual relationship between liquid surface tension and contact angle is studied and evaluated for aqueous solutions of these alcohols. Together with alcohols, the wetting properties of pure organic liquids and selected aqueous solutions of surface active agents are studied and compared. On behalf of the obtained results, the key properties of aqueous solutions of alcohols influencing the atypical wettability are discussed and evaluated.

2. Contemporary short view on wetting of solid surface

When a drop of a pure liquid is placed on a solid surface, it forms a characteristic shape described by the contact angle θ. In an ideal case, when a horizontal, flat and homogenous solid surface is assumed, Young's equation describes the equilibrium of solid–liquid–vapour interface.

$$\gamma_{SL} = \gamma_{SV} - \gamma_{LV} \times \cos\theta \qquad (1)$$

Here, γ_{SV}, γ_{SL} and γ_{LV} correspond to solid–vapour, solid–liquid and liquid–vapour interfacial tension, respectively. γ_{LV} is commonly called the surface tension of the liquid; γ_{SV} is sometimes equated with the surface free energies γ_S [4,10]. Moreover, γ_{SV} is often incorrectly equated with γ_{SG} (solid–gas interfacial tension). This can only be an approximate measure for non-volatile liquids. A deep analysis was given by Siboni [11]. For solid surface characterization, solid tension in a vacuum is often used too. The difference between this tension and γ_{SV} is then called "spreading pressure" π_e.

In Young's equation, only γ_{LV} and θ can be measured experimentally. Values of γ_{SV} and γ_{SL} can only be obtained indirectly. Fundamentally, they reflect the strength of molecular interactions within the bulk material [12]. Then γ_{SL} reflects the cross-interactions between two phases and may be derivable in terms of γ_{LV} and γ_{SV}. Historically, Zisman was the first to formulate what is his fundamental hypothesis of the so-called "critical surface energy γ_C". This method assumes that the contact angle of a liquid on a solid becomes zero when γ_{SV} and γ_{LV} are equal, and γ_{SL} is reduced to zero. The tension γ_{SV} is hereupon named "surface free energy of solid" [11] and it is denoted as γ_C. Experiments were carried out on fluorinated wax FC721 with a set of 13 organic liquids [13] and the difference $\gamma_{SV} - \gamma_{LV}$ (or $\gamma_{LV} \times \cos\theta$) was plotted against the surface tension of the liquids used. Here, the linear dependence of $\cos\theta$ on

γ_{LV} was assumed. However, according to recently published studies [11,14], the function $\cos\theta = f(\gamma_{LV})$ is not a straight line in the full range of liquid tensions; the linearity can be assumed only at the lowest surface tensions.

The majority of hitherto published studies have been devoted to the spreading of pure liquids even though in the majority of applications mixtures of liquids are used. The spreading of liquid mixtures is a very complex process depending primarily on its component properties [15]. Owing to their exceptional practical importance, the aqueous solutions of surface-active agents have been studied in detail for decades. When a surfactant molecule is dissolved in water, the free energy of the system increases. The system responds in order to minimize the contact between the surfactant hydrophobic group and the water [16]. As a result, some of the surfactant's molecules are expelled to the system interfaces. The transport processes take place on three interfaces: (i) surfactant adsorption at the inner liquid–solid interface resulting in a decrease of γ_{SL}, (ii) surfactant adsorption on the liquid–vapour interface resulting in a decrease of γ_{SV} and (iii) the transfer from the drop onto the solid–vapour interface just in front of the drop which hydrophilizes the initially hydrophobic surface. Moreover the surface tension gradient on the liquid–vapour interface causes liquid motion inside the drop (Marangoni flow) [17,18]. Due to the advancing transport of surfactant molecules, all mentioned processes are time dependent and the time evolution of the liquid drop spreading is observed [2]. The velocity of the surfactant transport to the liquid–vapour interface can then be studied by using the dynamic surface tension measurement for instance (e.g. maximum bubble pressure method).

The aqueous mixtures of short chain alcohols decrease the surface tension similarly as surfactants and, therefore, both types of mixtures are often equated. However, alcohol solutions exhibit some specific behaviour which depends on their microstructure. Alcohol and water molecules tend to develop the local microstructures in the bulk liquid and, moreover, the existence of a specific saturated microlayer on the solution-air interface is assumed. This internal structure significantly influences the interfacial properties, like surface tension or contact angle.

3. Experiments

3.1. Materials

A silanized glass and PTFE were used as model hydrophobic surfaces. The silanization method is based on the covalent attachment of functional organosilanes to silica or glass. Silanes are believed to react with the exposed hydroxyl groups of silanols on the glass surface and, under optimal conditions, they form a uniform monolayer [19]. In our project, the common type of silanized glass was used: the Silanization solution was supplied by Sigma–Aldrich (5% solution of dimethyldichlorosilane in heptane, CAS No. 75-78-5). The silanization method was applied according to recommendations from the literature [19]. The glass material (microscopic slides) was cleaned in a boiling mixture of sulphuric acid and hydrogen peroxide (1:1) for 1 min, then rinsed several times with distilled water and dried. The slides were dipped into the silanization solution for 24 h, then rinsed firstly with pure heptane then with acetone and ethanol in order to remove all organic residues, and finally they were dried. The silanized slides were stored in a dry place to avoid contact with air humidity. The surface homogeneity was tested using the AFM method. On clean glass, the maximum roughness reached a height of 60 nm (average 15 nm), and on silanized glass the maximum roughness reached a height of 160 nm (average 30 nm). The measurement was conducted within 1 week after preparation. Contact angles for pure water ranged from 103.1 to