



Surface tension of polytetrafluoroethylene and its wetting by aqueous solution of some surfactants and their mixtures



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ARTICLE INFO

Article history:

Received 25 July 2016

Received in revised form 2 September 2016

Accepted 7 September 2016

Available online 11 September 2016

Keywords:

Surfactants

Polytetrafluoroethylene

Contact angle

Adhesion work

Surface excess concentration

ABSTRACT

Measurements of the contact angle of aqueous solution of rhamnolipid (RL) mixture with n-octyl- β -D-glucopyranoside (OGP), Triton X-100 (TX-100) or/and sodium dodecylsulfate (SDS) on polytetrafluoroethylene (PTFE) were made. To this aim there was used a plate whose surface topography was analyzed by means of optical profilometry method. Additionally, plate surface chemistry was studied employing the Fourier transform infrared spectroscopy. The obtained values of contact angle were discussed based on the PTFE surface tension (γ_{SV}) as well as the Lifshitz-van der Waals component of the water surface tension (γ_W^{LW}). The contact angle of aqueous solution of several surfactants and their mixtures on PTFE was also considered on the basis of γ_{SV} and γ_W^{LW} . It occurred that by using the values of γ_{SV} , γ_W^{LW} and surface tension of the aqueous solution of surfactants and their mixtures, the contact angle on PTFE can be predicted. It also occurred that changes of adhesion tension of aqueous solutions of surfactants as a function of their concentration can be determined by the exponential function of the first or second order. Using such functions Gibbs surface excess concentration of surfactants at the PTFE-water interface, mole fraction of surfactant in the mixed monolayer and fraction of the area occupied by given surfactants in the monolayer were determined. Gibbs surface free energy of adsorption of a given surfactant in the presence of another one and adhesion work of the aqueous solution of surfactants to the PTFE surface were also evaluated.

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1. Introduction

Wettability of polytetrafluoroethylene (PTFE) is of significant importance for extensive practical applications [1,2]. Following the Young equation it can be stated that wettability of the solid depends on both the surface tension of solid and liquid and the solid-liquid interface tension [3,4]. A visual measure of solid wetting by a given liquid is the contact angle. As follows from the Young-Dupre equation [4] if there is a linear dependence between the adhesion and surface tension and its slope is equal to -1 , then the constant in the linear equation is equal to the adhesion work of liquids to the solid surface which is independent of the kind of liquid [5,6]. This can be often found in the PTFE-aqueous solution of the surfactant-air systems [5,7]. The linear dependence between adhesion and surface tension at the slope equal to -1 is also indicative of PTFE surface tension being constant in the whole range of surfactants concentration in the solution. On the other hand, according to the Lucassen-Reynders equation [8] there is comparable adsorption of

the surfactants or their mixtures at the PTFE-water and water-air interfaces. However, the dependence between adhesion and surface tension in the linear form is not indicative of the changes of the PTFE-solution interface tension as a function of surfactants concentration. Thus the value of the solution surface tension determined from this dependence for the contact angle equal to zero is called the critical surface tension of solid wetting [9]. This value is not equal to the PTFE surface tension in every case as the PTFE-solution interface tension for the contact angle equal to zero can be different from zero [10,11]. Thus it was difficult to predict exactly contact angle values on the basis of the PTFE and solution surface tension and their components. However, the literature reports different values of PTFE surface tension [10–26]. In most cases they were determined from the contact angle measurements of different liquids. Generally, it can be stated that the values of PTFE surface tension determined from the contact angle for polar liquids are significantly different from those determined from the contact angle for apolar ones [14,25]. The PTFE surface tension evaluated from the contact angle values depends also on the approach to the interfacial tension used in the Young equation [14,15,22,25]. The literature reports many different approaches to this tension. Those of van Oss et al. [3,27,28] and Neumann et al. [21–24] are the

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most commonly applied for solids surface tension determination. The van Oss et al. approach [3,27,28] assumes that the interfacial tension depends on the Lifshitz-van der Waals component and the electron-acceptor and electron-donor parameters of the Lewis acid-base component of the substrates being in contact. To study changes of the contact angle of surfactants aqueous solutions as a function of their concentration, it is necessary to know water surface tension components and parameters. Fowkes [12] as the first calculated the dispersion component of water surface tension to be equal to 21.8 mN/m at 293 K from the *n*-alkane-water interface tension. In turn, van Oss et al. [3,27,28] assumed this value to be the Lifshitz-van der Waals component of water surface tension. However, the difference between the surface tension and this component was treated as the Lewis acid-base one being the function of electron-acceptor and electron-donor parameters equal to 25.5 mN/m [3,27,28]. Almost all investigators assume that PTFE surface tension results only from the Lifshitz-van der Waals intermolecular interactions. If so, the value of the surface tension of PTFE determined from the van Oss et al. [3,27,28] approach using the contact angle for water on its surface should not differ from that obtained for apolar liquids. However, in all cases difference between the values of PTFE surface tension calculated from the contact angle for water and apolar liquids can be observed. Probably this provides difficulties in precise prediction of contact angle on the PTFE surface of aqueous solution of surfactants and their mixture from the PTFE surface tension determined from the contact angle for apolar liquids and solution surface tension. Indeed, both the surface tension of aqueous solutions of surfactants and their mixture and the PTFE-solution interface tension depend on the surfactants adsorption at the water-air and PTFE-water interfaces as well as orientation of their molecules at these interfaces.

Thus the purpose of our paper was to explain why different values of PTFE surface tensions were obtained from the contact angle for water and apolar liquids and to establish parameters on the basis of which it can be possible to predict the contact angle of the surfactants and their mixture on PTFE surface as well as the adsorption of the RL with OGP, TX-100 and SDDS mixtures at the PTFE-water interface. For this purpose there were applied the measured values of the contact angle of aqueous solutions of the above mentioned surfactants mixtures, the literature values of the contact angle for the aqueous solution of individual surfactants and their mixtures as well as those of surfactants and short chain alcohols.

2. Experimental

2.1. Materials

N-octyl- β -D-glucopyranoside (OGP) (SIGMA-ALDRICH) (purity >98%) and R-95 Rhamnolipid (SIGMA-ALDRICH) (purity 95%), sodium dodecylsulfate (SDDS) (Merck) (purity >98%), *p*-(1,1,3,3-tetramethylbutyl)phenoxy polyoxyethylene glycol, Triton X-100 (TX-100) (SIGMA-ALDRICH) (purity >99%) were used without further purification. The aqueous solutions were prepared using doubly distilled and deionized water (Destamat Bi18E). Its purity was additionally controlled by the surface tension measurements before preparing the solutions. Series of aqueous solutions of RL with SDDS, RL with TX-100 and RL with OGP mixtures were prepared at a constant concentration of one surfactant. The RL concentration (C_1) was in the range from 3.97×10^{-10} M to 7.94×10^{-5} M, for SDDS from 1×10^{-8} to 1×10^{-2} M, for TX-100 from 1×10^{-8} to 2×10^{-3} M and for OGP from 1×10^{-5} to 5×10^{-2} M.

The contact angle was measured using polytetrafluoroethylene (PTFE), (Mega-Tech, Poland) plates. They were washed sequentially with a detergent and next with methanol, placed in an ultrasonic

bath in the Milli-Q water twice for 15 min and dried in the desiccator at room temperature. The quality of each plate surface was monitored using a polarizing microscope (Nikon, ECLIPSE E 600 POL) but the surface topography of PTFE and each plate roughness were analyzed using an optical profilometer (Contour GT, Veeco). For the contact angle measurements, the plate whose the rms roughness was the smallest was chosen. In turn, surface chemistry of PTFE was studied by means of Fourier transform infrared (FT-IR) spectroscopy in order to identify a kind of surface functional groups. The FT-IR spectrum was recorded on a 1725X Perkin-Elmer spectrophotometer at room temperature with a resolution of 4 cm^{-1} and KBr discs.

2.2. Measurements of contact angle

Firstly, measurements of the advancing contact angles for pure water on the PTFE surface were made using the sessile drop method, DSA30 measuring system (Krüss), in a thermostated chamber at 293 ± 0.1 K and Wilhelmy plate (Krüss K100C).

Advancing contact angles of aqueous solutions of RL with OGP, SDDS or TX-100 mixture on the PTFE surface were measured using the sessile drop method. The chamber of apparatus was saturated by vapour of a given liquid for which the contact angle was measured placing a cell filled with a given liquid a few hours before the measurements. The contact angle for a given liquid was measured for at least 30 drops and good reproducibility was found. The standard deviation for each set of values was less than 1.2° .

2.3. Profilometer images of PTFE surface

One of the factors affecting wettability of solids is their roughness. The impact of surface roughness is especially important in term of hydrophobic surfaces and hydrophilic liquids like water because such liquids do not penetrate rough surface asperities [29] and therefore surface free energy of materials can be reduced if air is trapped below the drop of liquid [30]. From this reason the 2D image of PTFE surface and the roughness side profiles along the *x* and *y* axes were made and presented in Fig. 1. The average roughness (R_A) for the PTFE plate is equal to $0.197 \mu\text{m}$, the root mean square parameter (R_{RMS}), which expresses the standard deviation of the surface height distribution is equal to $0.262 \mu\text{m}$ and the max profile height (R_t) to $5.605 \mu\text{m}$. Thus it follows from the profilometer image that PTFE surface roughness should only insignificantly influence on contact angle values.

2.4. FT-IR spectra of PTFE

Fig. 2 shows the FT-IR spectra for PTFE. The studied polymer has no C–H groups in its structure. Therefore, weak bands around $2800\text{--}2950 \text{ cm}^{-1}$ in the C–H stretch region are probably due to contaminations on the PTFE surface. The most intense bands around 1150 cm^{-1} and 1200 cm^{-1} are assigned to $-\text{CF}_2-$ stretching vibrations. The sample exhibits two very weak peaks around 1010 cm^{-1} and 1050 cm^{-1} which can be attributed to the $-\text{CF}_3$ stretching vibrations. In the region of $500\text{--}750 \text{ cm}^{-1}$ there are several bands characteristic of different types of CF_2 -groups deformation vibrations e.g. rolling, twisting, wagging and rocking ones.

3. Results and discussion

3.1. Surface tension of PTFE and contact angle of aqueous solution of surfactants

Surface tension of PTFE determined from the contact angle for *n*-alkanes in the homologous series from *n*-heptane to *n*-hexadecane

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