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Some remarks on the solid surface tension determination from contact angle measurements

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A B S T R A C T

The measurements of water, formamide and diiodomethane contact angle (θ) on polytetrafluoroethylene (PTFE), polyethylene (PE), polymethyl methacrylate (PMMA), nylon 6, quartz and silica were performed. Based on the θ values of these liquids obtained on PTFE, the Lifshitz-van der Waals and acid-base and/or dispersion and polar components of their surface tension (ST) were determined. In turn, the θ values for water, formamide and diiodomethane on PMMA were applied to calculate the electron-acceptor and electron-donor parameters of the Lewis acid-base component of the formamide ST. For this calculation the same values of the electron-acceptor and electron-donor parameters for water ST were used. Taking into account the values of components and parameters of water, formamide and diiodomethane ST obtained by us, van Oss et al. and from the water(formamide)-n-alkane and water-diiodomethane interface tension, the components and parameters of studied solids ST were calculated. To this end different approaches to the interface tension were considered. The obtained values were compared with those in the literature. It was concluded that for determination of solid ST components and parameters, those of water, formamide and diiodomethane ST obtained from the θ measurements on the model solids should be used.

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1. Introduction

Surface tension of solids and liquids as well as their components and parameters play an important role in the processes in which adhesion, adsorption, wettability and aggregation take place [1–6]. However, determination of solid surface tension encounters many difficulties. It is possible to find a few direct methods of surface tension measurements as well as theoretical calculations based on the free energy of chemical bonds and the most indirect methods based on the contact angle, adsorption and heat of immersion measurements [1,2,6,7]. Of the indirect methods the one based on the contact angle measurements of model liquids on the solid surface is the most often used for determination of surface tension of solids and their components and parameters.

In the literature it is possible to find many methods of contact angle value on the solid flat surface evaluation [8]. Among them those based on the shape of a settled drop in the solid-liquid drop-air system are the most frequently used. However, it is not easy to determine the value of contact angle in the three phase contact point. In the literature from a direct method based on the telescope-goniometer system there can be found numerous the-

oretical methods of contact angle value evaluation from the drop shape. Among other things, they take into account tangential fitting, circle fitting, ADSA or polynomial fitting to drop profile [9–11].

The main problem regarding using contact angle values for components and parameters of solid surface tension determination is establishing relationships between the solid-liquid interface tension and surface tension of solid and liquid.

The first who divided the surface tension of liquids and solids into many components resulting from different intermolecular interactions was Fowkes [7,12]. From the practical point of view it was possible to establish two components: dispersion and polar ones. Fowkes deduced that the surface tension of n-alkanes results only from dispersion intermolecular interactions and proved that the work of adhesion of n-alkanes to the water surface is a function of the geometric mean of the surface tension of n-alkanes and the dispersion component of water surface tension [7,12]. Based on this he determined the dispersion component of water surface tension as equal to 21.8 mN/m at 293 K. The other authors determined the dispersion component of formamide and diiodomethane surface tension in the same way [13]. These liquids are commonly used as model ones for determination of solid surface tension from the contact angle measurements [2].

Contrary to Fowkes, van Oss et al. [2,14–17] divided solids and liquids surface tension into the Lifshitz-van der Waals and Lewis acid-base components. Simultaneously, they expressed the Lewis

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acid-base component as a function of geometric mean from the electron-acceptor and electron-donor parameters. To determine components and parameters of liquids and solids, one reference liquid is needed. Van Oss et al. [2,16,17] chose water as the reference liquid assuming that the value of dispersion component of its surface tension determined by Fowkes and equal to 21.8 mN/m is equal to the Lifshitz-van der Waals one, and the difference between the water surface tension equal to 72.8 mN/m and 21.8 mN/m expresses the acid-base component. They also assumed that electron-acceptor and electron-donor parameters of the acid-base component of water surface tension are the same and equal to 25.5 mN/m.

The Lifshitz-van der Waals component of formamide surface tension was established from the contact angle on the apolar solid whose surface tension results from the Lifshitz-van der Waals intermolecular interactions. Next, by measuring the contact angle of diiodomethane, water and formamide, the electron-acceptor and electron-donor parameters of the Lewis acid-base component of formamide surface tension were determined. It proved that the components and parameters of formamide surface tension determined in such a way are considerably different from those determined on the basis of liquid-formamide interface tension [2,13,16,17]. Therefore it seems that for determination of components and parameters of solids surface tension all of these magnitudes for model liquids should be determined in the same way.

This problem was the main purpose of our studies. That is why we measured the contact angle of water, formamide and diiodomethane on the polytetrafluoroethylene (PTFE), polyethylene (PE), polymethyl methacrylate (PMMA), polyamide (nylon 6), quartz and silica surfaces and analyzed the obtained results in the light of components and parameters of water, formamide and diiodomethane surface tension. The usefulness of these magnitudes determined in different ways was tested calculating the surface tension and its components as well as parameters of the mentioned solids. The surface tension values calculated from the van Oss et al. [2,16,17] and Owens and Wendt [18] approaches to the interface tension were also compared to those determined from the Neumann et al. equation [19–22]. As it is known Neumann et al. [19–22] do not assume distribution of liquid and solids surface tension into components.

2. Experimental

2.1. Materials

For the contact angle measurements of water, formamide and diiodomethane, polytetrafluoroethylene (PTFE), polyethylene (PE), polymethyl methacrylate (PMMA), polyamide (nylon 6), quartz (Quartz I, Quartz II and Quartz III) and silica (Si ($\langle 110 \rangle$) and Si ($\langle 111 \rangle$)) were used. Water was doubly distilled and deionized (Destamat Bi18E). Its resistance was equal to 18.2Ω. Formamide (purity > 99.5%) and diiodomethane (purity >99%) were bought from Sigma-Aldrich. The surface tension of the liquids at 293 ± 0.1 K was tested using the Wilhelmy plate (water 72.85 ± 0.1 mN/m, formamide 57.95 ± 0.09 mN/m, diiodomethane 50.77 ± 0.07 mN/m) and the du Noüy ring method (water 72.75 ± 0.11 mN/m, formamide 58.05 ± 0.08 mN/m, diiodomethane 50.82 ± 0.08 mN/m) (tensiometer K100, Krüss). As the surface tension data controlled by us were very close to the literature ones, only the literature were applied in our calculations [2,7,13]. The polymer plates (50 mm × 30 mm) were cut from planes obtained from Mega-Tech, Poland. Before measurements the polymer plates (PTFE, PE, nylon 6) were polished with a light pressure on a Buchler polishing wheel using a clean, dry, silk polishing cloth. These plates were

washed sequentially with a detergent and next with methanol, placed twice in an ultrasonic bath in the Milli-Q water for 15 min and dried in the desiccator with a molecular sieve at room temperature. The silica plates of the crystallographic structure $\langle 110 \rangle$ and $\langle 111 \rangle$ and controlled level of oxygen in the silicon single crystals of 5.5–10×10^{17} atoms/cm³ were bought from the Department of Silicon Technology, Institute of Electronic Materials Technology in Warsaw (Poland). Quartz solids were obtained from Conductance, Poland. Silica plates were etched by the manufacturer in the acid or alkaline mixture. Quartz and silica plates were cleaned with soapy water, washed in distilled water many times and placed in the ultrasonic bath for 15 min. This procedure was repeated twice for each plate. Then the plates were dried and placed in the desiccator with molecular sieves.

The surface topography of chosen plates was monitored using an optical profilometer (Contour GT, Veeco) and atomic force microscopy (AFM) (Nanoscope 3, VEECO). For the contact angle measurements, the plate with the smallest roughness was used. The surface chemistry of solid surfaces was determined using the Fourier transform infrared (FT-IR) spectroscopy. The FT-IR spectrum was recorded on a 1725X Perkin-Elmer spectrophotometer at room temperature with a resolution of $4\,cm^{-1}$.

2.2. Surfaces characterization

Figs. 1–5 show the characteristics of the PTFE, PE, PMMA, nylon 6 and quartz surfaces using AFM and the profilometer technique as well as their FT–IR spectra. As roughness of the silica surfaces was characterized by a manufacturer ($R_a < 5\,Å$), they were not further characterized. For the PTFE surface (Fig. 1) there are very intense bands around $1115\,cm^{-1}$ and $1200\,cm^{-1}$ assigned to $-CF_2$ stretching vibrations. In the region of 505–$640\,cm^{-1}$ there are several bands characteristic of different types of $-CF_2$ groups deformation vibrations e.g. rolling, twisting, wagging and rocking. The most intense spectral features of PE (Fig. 2) occurring between 2850 and $2915\,cm^{-1}$ are simplified as the fundamental C—H stretching vibrations. There are also quite weak bands around 1460–$1470\,cm^{-1}$ referring to the $-CH_2$ deformation vibrations, as well as around 720–$735\,cm^{-1}$ attributed to the $-CH$ ones out of the binding plane. As follows from the FT–IR spectra of PMMA (Fig. 3), there are strong bands around 2950–$2990\,cm^{-1}$ in the C—H and $1720\,cm^{-1}$ in the C=O stretching vibration regions. Also strong bands around 1385–$1480\,cm^{-1}$ corresponding to the $-CH_2$ and $-CH_3$ deformation vibrations are observed. In turn, the FT–IR spectral region around 1060–$1230\,cm^{-1}$ and 750–$990\,cm^{-1}$ refers to the C—O stretching and C—H deformation vibrations. In the FT–IR spectra of nylon 6 (Fig. 4) in the region around $3300\,cm^{-1}$ there is a strong band from the N—H stretching vibrations, and around 2850 and $2920\,cm^{-1}$ there are two strong bands from the C—H stretching vibrations. In turn, in the region around $1630\,cm^{-1}$ and 1170–$1370\,cm^{-1}$ there are strong bands resulting from the C=O and C—N stretching vibrations, respectively. In the region around $1540\,cm^{-1}$ there is a very strong band from the N—H deformation vibrations, and 1415–$1470\,cm^{-1}$ a multiple band from the $-CH_2$ and $-CH_3$ deformation ones is found. As follows from Fig. 4, the bands in the spectral region around 520–$690\,cm^{-1}$ refer to the C—C or C—H deformation vibrations. Taking into account the PMMA and nylon 6 FT–IR spectra, it can be stated that the quantity of the C=O groups on these surfaces is comparable. In the case of the quartz surfaces (I, II and III) the first band around $985\,cm^{-1}$ and $785\,cm^{-1}$ is characterized as asymmetric Si—O—Si and symmetric Si—O—Si stretching vibrations [23,24]. The second quite strong band, specified as O—Si—O deformation or bending modes, occur in the spectral region of 400–$430\,cm^{-1}$. There are no significant differences between the FT-IR spectra of quartz I, II or III. However, some