Applied Surface Science 257 (2011) 7959–7967

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

# Adsorption behavior of weak hydrophilic substances on low-energy surface in aqueous medium

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ARTICLE INFO

*Article history:*
Received 22 January 2011
Received in revised form 1 March 2011
Accepted 31 March 2011
Available online 8 April 2011

*Keywords:*
Weak hydrophilic substances (WHS)
Adsorption
Low-energy surface (LES)
Contact angle
Surface energy

ABSTRACT

Through the methods such as measurements of contact angle and surface tension, calculations of surface energy and interfacial interaction free energy, and four weak hydrophilic substances (WHS) were taken as research objects, some interesting conclusions were obtained as follow. In aqueous medium, the WHS give priority to adsorb on low-energy surface that is low polar or particularly non-polar. There is a clear corresponding relationship between the free energy and Lewis base component $\gamma^-$ or the hydrophile index of low-energy surface, and the specific relationship is obtained. Finally, we find hydrophobic attractive force of the Lewis acid–base interaction is mainly responsible for the absorption of WHS on low-energy surface. In short, an initial insight into adsorption behavior of WHS on low-energy surface is demonstrated in this paper.

## 1. Introduction

Low-energy surface (LES) attracted increasing attention in recent decades [1–5]. Weak hydrophilic substances, WHS for short, are used very commonly as frother in flotation to assure formation of a foam having a definite properties [6]. However, it is still unclear about their adsorption behavior on LES (surface energy of LES is usually below 100 mJ m$^{-2}$, and for polymer is usually between 20 and 50 mJ m$^{-2}$) in aqueous medium. We conducted this study to solve the question deserving attention whether the effect of WHS adsorption can be neglected or not, in order to deal with system of adsorption of WHS on LES such as plastic [7], coal [8–10], molybdenite [11], graphite [12–14], talc flotation [15–17] and oil production [18–20], oil displacement process [20–22]. Garde and co-workers [23] had found that the adsorption free energies of a low-energy probe shows a clear correlation with the hydrophobicity of the interface. It is clear that inorganic minerals have high-energy surface subject to strong adsorption by solutes and establishment of stabilizing electrical forces for flotation. Plastics have LES, unlikely to adsorb solutes or form any kinds of electrical stabilizing forces for flotation [24]. About plastics flotation, Fraunholcz [25] had discussed the liquid-vapour surface tension control method. Methyl isobutyl carbinol (MIBC) [26] was used as frother to separate mixed post-consumer PET–POM–PVC. Pine oil and MIBC were used together as frother to separate PVC/PET mixtures [27]. Clint et al. [28] indicated that the order of strengths of adhesion of “liquid” to solid surface under water is opposite to that for adhesion in air. Lee [29] used $\gamma^+/\gamma^- = 1.8$ at 20 °C and concluded that $\gamma^{LW}$ components and $\gamma^{AB}$ components and total surface free energy were not affected [30,31]. Della Volpe et al. [32] discussed the results between surface tension component acid–base theory and equation-of-state theory, and they also explained why square root of a specific energy is better [33]. Wang Hui et al. [34] determined the Lifshiitz–van der Walls and the Lewis acid–base components of the LES energy parameters. Which one is main responsible for the absorption of WHS on LES in aqueous medium, between the Lifshitz–van der Waals [35–37] and the Lewis acid–Base interaction [38,39], is another question we will answer. On the whole, our researches were performed to get an initial insight into adsorption behavior of weak hydrophilic substances on LES in aqueous medium.

## 2. Materials and methods

### 2.1. Materials

Common flotation frothers are low molecular weight surfactant. Solubility of frothers in water, different from wetting agent, is usually limited, and overall they are weak hydrophilic [40]. Four frothers are selected as study object in this paper: Terpineol (TP), Methyl isobutyl carbinol (MIBC), Tripropylene glycol n-butyl ether (TPnB) and Diethyl o-phthalate (DOP). Chemical structures and some information of them are shown in Table 1.

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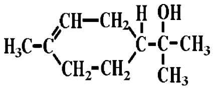
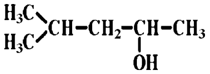
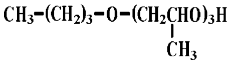
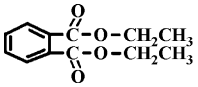
doi:10.1016/j.apsusc.2011.03.158

**Table 1**
Four frothing agent selected as study object.

| Weak hydrophilic substance | | Appearance and property | Chemical structure | Purity | Manufacturer |
|---|---|---|---|---|---|
| Agent | Terpineol, TP | Colorless and transparent oily liquid |  | Analytical pure | Chem. Reagent Fty of Hunan Normal University |
| | Methyl isobutyl carbinol, MIBC | Colorless and transparent oily liquid |  | Industrial products | Zhuzhou flotation reagent fty |
| | Tripropylene glycol n-butyl ether, TPnB | Colorless and transparent oily liquid |  $CH_3-(CH_2)_3-O-(CH_2\underset{CH_3}{CH}O)_3H$ | Industrial products | Zhuzhou flotation reagent fty |
| | Diehyl o-phthalate, DOP | Colorless and transparent oily liquid |  | Analytical pure | Guangdong Xilong chem. CO., Ltd. |

Contact-angle measurements were used for determining the solid surface-energy. The test liquids include double distilled water, glycerol, formamide, diiodomethane and ethylene glycol (all are analytical purity).

## 2.2. Methods

### 2.2.1. Membrane surface preparation

Before conducting surface inspection, each low-energy plate (mainly are the latter 35 different kinds of material) was cut into 20 × 20 mm, and protective membranes were torn off, then they was put into tap water containing washing powder, tap water, distilled water in sequence to clean for 10 min in ultrasonic generator (Shanghai Ultrasonic Co. Ltd., China). Take them out and rinse in distilled water for 5 min, then put them on filter paper to dry at room temperature, finally put them together with the filter paper into silica gel dryer (pre-dried 2 h at 150 °C) and dry for 24 h.

Membrane surface is prepared in order to detect nonionic frothers and surface energy properties of material treated by frothers. The "soaking method" was used for making a surface film of the frother (TP, MIBC, TPnB and DOP). A blank copperplate paper was cut to 20 mm × 20 mm and dipped into the frother solution for about 1 min and then stored in a silica gel desiccator for about 24 h before use, and other membrane treated by frothers is prepared in the same way.

### 2.2.2. Measurements of contact angle and surface tension

A JJC-I contact angle measuring instrument (Changchun Optical Instrument Factory, China) is applied to measure the contact angle of liquid on the solid surface. When measuring, at the distance of 3 mm above solid, the liquid is vertical, carefully dropped onto a solid surface to form a sessile drop by micro-injector (2.0 mL). Make sure the droplet size is 3.5 μL, diameter is 1–2 mm, and measuring time is less than 1 min. Ten measurements were taken, and an average value was reported. All measurements were conducted at room temperature, generally 25 °C.

Liquid surface tension is measured by Du Nouy rings method, and the apparatus is type JZHY-180 interface tension meter (Hebei Chengde Test Machine Factory, China). Measurements were conducted at room temperature. The glass used to contain the liquid was washed by solution prepared by potassium bichromate and sulfuric acid, and then repeatedly washed with distilled water for 5 times. When measuring, measured liquid is consumed 20–25 mL each time. Ten measurements were taken, and an average value was reported.

### 2.2.3. Calculation of surface energy

Young's Equation [41] describes the relationship among solid surface energy $\gamma_S$, liquid surface energy (surface tension) $\gamma_L$, solid–liquid interface interaction free energy $\gamma_{SL}$, solid surface membrane pressure $\pi^0$ and the equilibrium contact angle ($\theta$) in solid/liquid/gas three-phase system (Eq. (1)).

$$\gamma_S - \pi^0 - \gamma_{SL} = \gamma_L \cos\theta \qquad (1)$$

For the LES, surface membrane pressure $\pi^0$ is negligible [42], and Young's Equation is transformed into Eq. (2).

$$\gamma_S - \gamma_{SL} = \gamma_L \cos\theta \qquad (2)$$

van Oss et al. [43,44] deemed that solid or liquid surface energy $\gamma$ is composed of Lifshitz–van der Waals component $\gamma^{LW}$ and Lewis acid–base components $\gamma^{AB}$ that is composed of Lewis acid component $\gamma^+$ and Lewis base component $\gamma^-$. Thus, for solid or liquid, surface energy can be expressed as Eq. (3) and Eq. (4), respectively.

$$\gamma_S = \gamma_S^{LW} + \gamma_S^{AB} = \gamma_S^{LW} + 2\sqrt{\gamma_S^+\gamma_S^-} \qquad (3)$$

$$\gamma_L = \gamma_L^{LW} + \gamma_L^{AB} = \gamma_L^{LW} + 2\sqrt{\gamma_L^+\gamma_L^-} \qquad (4)$$

Relationship between solid–liquid interface interaction free energy and surface energy of solid and liquid, respectively, can be expressed as Eq. (5).

$$\gamma_{SL} = \left(\sqrt{\gamma_S^{LW}} - \sqrt{\gamma_L^{LW}}\right)^2 + 2\left(\sqrt{\gamma_S^+\gamma_S^-} + \sqrt{\gamma_L^+\gamma_L^-} - \sqrt{\gamma_S^+\gamma_L^-} - \sqrt{\gamma_S^-\gamma_L^+}\right) \qquad (5)$$

Expressing the Eq. (2) in the form of Eqs. (3)–(5) gives the relationship in solid surface-energy, liquid surface-energy and the equilibrium contact angle between the two are obtained (Eq. (6)).

$$\left(\gamma_L^{LW} + 2\sqrt{\gamma_L^+\gamma_L^-}\right)(1+\cos\theta) = 2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^+\gamma_L^-} + \sqrt{\gamma_S^-\gamma_L^+}\right) \qquad (6)$$

Thus, through measuring the contact angle between the solid surface and three liquids (two of which must be polar) whose $\gamma_L^{LW}$, $\gamma_L^+$, $\gamma_L^-$ are known, parameters of solid surface energy can be obtained ($\gamma_S^{LW}$, $\gamma_S^+$, $\gamma_S^-$). Detected liquid used in experiment includes secondary distilled water, glycerol, formamide, diiodomethane and ethylene glycol. There are many reports on parameters of the surface energy about these liquid (Table 2) from literature [45–47].