Contents lists available at ScienceDirect

Colloids and Surfaces A

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

Research Paper

Characterisation of acid–base surface free energy components of urea–water solutions



Alexandros Terzis^{a,*}, Elmar Sauer^b, Guang Yang^{a,c}, Joachim Groß^b, Bernhard Weigand^a

^a Institute of Aerospace Thermodynamics (ITLR), Pfaffenwaldring 31, University of Stuttgart, 70569 Stuttgart, Germany

^b Institute of Thermodynamics and Thermal Process Engineering (ITT), Pfaffenwaldring 9, University of Stuttgart, 70569 Stuttgart, Germany

^c Institute of Refrigeration and Cryogenics, Shanghai Jiao Tong University, 200240 Shanghai, China

G R A P H I C A L A B S T R A C T



ARTICLE INFO

Keywords: Urea-water-solutions Contact angle measurements Acid-base interfacial interactions Wetting

ABSTRACT

The objective of this study is to determine the Lifshitz–van der Waals/Acid–Base (LW/AB) surface energy components of urea–water-solutions (UWS) for different urea mass fractions. The surface energy parameters are evaluated by ring tensiometry and contact angle measurements of sessile drops placed onto pre-determined solid substrates. Therefore, the energetic characteristics of UWS are evaluated in relation to probe liquids. The results indicate that aqueous solutions of urea become less polar with increasing urea mass fraction while their overall surface tension is also increased. This is attributed to a significant grow of the Lifshitz–van der Waals surface energy component that compensates the reduction of the polar part. In addition, aqueous solutions of urea are characterised by a significant electron donor (γ_l^-) capacity compared to pure water while their electron acceptor parameter (γ_l^+) is reduced. Subsequently, γ_l^+/γ_l^- is continuously reduced with increasing urea concentration. The enhancement of electron-donicity is also reflected to the pH of the solutions while the overall trends are independent from the selection of acid-to-base ratio for pure water. The above findings are related to physico-chemical aspects based on molecular and intermolecular interactions.

1. Introduction

Aqueous solutions of urea are nowadays widely used covering a

broad range of applications varying from biological processes, such as urea induced protein denaturation [1–3], to engineering applications and the reduction of NO_x emissions for automotive diesel engines [4–6].

* corresponding author. *E-mail address:* alexandros.terzis@me.com (A. Terzis).

https://doi.org/10.1016/j.colsurfa.2017.11.068 Received 23 October 2017; Received in revised form 23 November 2017; Accepted 24 November 2017 Available online 26 November 2017 0927-7757/ © 2017 Elsevier B.V. All rights reserved.



However, the protein denaturation mechanism in terms of interactions in aqueous urea media is not sufficiently understood, driving many studies to focus on the effect of urea on the molecular structure of the surrounding water [7-10]. Accordingly, the most crucial factor in exhaust aftertreatment systems is the mitigation of solid deposit formation [11-13], which is a direct consequence of urea crystallization that is initiated at the solid–liquid interface and depends on the wettability of the aqueous urea droplets [14].

Despite their ubiquitous use in colloid and interface science research, a fundamental property of urea-water-solutions (UWS) that has not been studied in detail so far, is their surface free energy as influenced by intermolecular interactions in condensed phase systems. The only surface energy values reported in the literature for many years concerned a 0.325 urea mass fraction solution from Birkhold et al. [5], 75 mJ/m² at 20 °C, and the company BASF [15], 65 mJ/m² at 25 °C, leading to an uncertain illustration of whether UWS have higher surface-free-energy (SFE) than water or not. Recently, Halonen et al. [16] clearly showed that the surface tension of UWS increases with urea concentration explaining the trend to the larger number of hydrogen bonds between urea and water molecules. However, molecular dynamic simulations indicated that urea-water hydrogen bonds are weaker compared to water-water interactions while the total number of hydrogen bonds of the solution remains nearly unchanged [8,9]. This leads to an overall reduction of the total hydrogen bond energy. There are also indications that urea does not change [7] or slightly increases [17,8] the hydrogen bond strength between water molecules. In addition, contact angles of urea-water binary droplets on graphitic surfaces provided lower values compared to pure water with a tendency of increasing wettability with urea mass fraction [18].

Two very interesting questions are now raised: (1) why the surface tension of UWS is higher than water and increases with urea concentration given that the overall hydrogen bond energy of the solution is decreased, and (2) assuming that the contact angles of different UWS on low-energy solids follow a regular pattern ("equation of state" approach.¹From Young's equation can be therefore concluded that for a given solid, as γ_l is increased the product $\gamma_l \cos\theta$ monotonically decreases resulting the so called "regular pattern" of contact angles.

[19–22]), how it is possible that the contact angle on a low-energy graphitic surface is reduced with urea concentration given that the total surface tension is increased. Regarding the latter, it has been clarified that contact angle interpretations of surfactant solutions or binary mixtures of liquids are complicated due to preferential adsorption on the solid that breaks the regular pattern validity [23,19]. This was also shown by molecular dynamic simulations which indicated that urea molecules in an aqueous droplet tend to be relocated according to the hydrophilicity of the substrate [18]. Kwok and Neumann [20] stated that Young's equation is still applicable in this case, however, no wettability theory (or in particular, the "equation of state" approach) can be used to determine the solid–liquid interfacial energy (γ_{sl}).

A multi-component surface energy theory, on the other hand, introduces additional unknowns to the already underdetermined Young's equation. However, the classification of surface energy components according to intermolecular interactions, as an extension of Fowkes approach [24], may allow the use in aqueous solutions. To the best of our knowledge, the only published literature source that includes such information is a technical report from KRÜSS company [25]. This considers the two-component surface energy theory of Owens-WendtRabel-Kaelble (OWRK).²where superscripts D and P account for the dispersive (van der Waals) and polar (e.g. hydrogen bonding) interactions, respectively.

[26,27] to show that a small addition of ethanol to water, e.g. 2%, significantly reduces the polar component of surface energy while leaving the dispersive one nearly unchanged. From a physicochemical point of view, this makes sense. Ethanol is significantly less polar than water due to the fewer hydrogen bond opportunities between adjacent molecules. Similarly, the propensity to Lewis acid/base interactions can be also evaluated based on the semi-empirical expression of van Oss-Chaudhury-Good (vOCG) [28,29], which further divides the polar part of surface energy in the non-additive, electron-donor and electron-acceptor parameters. This approach successfully described adsorption processes on activated carbons [30,31] and proteins in aqueous media [32], as well as exothermic capillary filling of cellulosic micro-substrates [33]. Apparently, multi-component surface energy theories, although thoroughly criticised for their mathematical validity [34,20], may provide useful information when treated correctly.

The objective of this study is to investigate an unexplored but important parameter concerning interfacial interactions in urea aqueous media. Using the vOCG approach, the Lifshitz–van der Waals (γ_l^{LW}), electron-donor () and electron-acceptor (γ_l^+) parameters of urea–water-solutions are determined by surface tension and contact angle measurements. Three different urea mass fractions, 0.16, 0.33 and 0.5 are investigated and the results are related to physicochemical aspects according to intermolecular interactions.

2. Materials and methods

2.1. Urea water solutions (UWS)

The urea–water-solutions are the result of mixing distilled water with pure urea for molecular biology from AppliChem GmbH (1.323 g/ cm³, 60.06 g/mol). Three different aqueous urea solutions were prepared with concentrations 16.6%, 33% and 50% by weight. After mixing, and due to the negative heat of solution [35], the UWS were left to equilibrate at room temperature. The density of the solutions, which is an important input for the ring tensiometry, was determined by weighting 200 mL of liquid on an APTP-452 digital scale (\pm 0.01 g). The densities for 0.166, 0.333 and 0.5 urea mass fractions were 1.043 g/cm³, 1.084 g/cm³ and 1.121 g/cm³, respectively.

2.2. van Oss-Chaudhury-Good (vOCG) approach

The vOCG surface tension theory [28,29,32] divides the surface free energy of a material (i = solid or liquid) into the additive Lifshitz–van der Waals (LW) and Lewis Acid/Base (AB) components:

$$\gamma_i = \gamma_i^{\rm LW} + \gamma_i^{\rm AB} \tag{1}$$

where γ_i^{LW} includes all electrodynamic contributions dominated by dispersion forces, and γ_i^{AB} the acid–base interactions including hydrogen bonding. This shows that dispersive and acid–base interactions are independent of each other in analogy to OWRK approach. However, γ_i^{AB} further incorporates the electron-donor γ_i^- and electron-acceptor γ_i^+ parameters as follows:

$$\gamma_i^{\rm AB} = 2\sqrt{\gamma_i^- \gamma_i^+} \tag{2}$$

van Oss et al. deduced this expression since Lewis acid-base interactions are asymmetrical, and hence, cannot be additive. From Eq. (1), Eq.

```
\gamma_l = \gamma_l^D + \gamma_l^P
```

¹ The equation-of-state approach considers empirical equations in order to calculate the solid–liquid interfacial energy, e.g.:

 $^{^2}$ According to OWRK theory, the surface tension of a liquid can be divided into two individual components according to intermolecular interactions:

Download English Version:

https://daneshyari.com/en/article/6978012

Download Persian Version:

https://daneshyari.com/article/6978012

Daneshyari.com