Thin Solid Films 541 (2013) 32–35

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

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

Optical spectroscopy used to investigate water evaporation rate from aqueous solutions

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ARTICLE INFO

Available online 5 January 2013

Keywords:
Optical spectroscopy
IR-ATR
Water evaporation
Glycol
Hydrogen bond
Diffusion
Relaxation time

ABSTRACT

Evaporation of water is a fundamental process in many technologies for film fabrication from liquid phase and, in the last decade, in nanoscience by the evaporation induced self assembly phenomena. Although the water evaporation seems to be among the very basic physical phenomena, there is a lack of experimental data that could enrich our understanding of this process.

Aqueous solutions of glycols and some amphiphilic molecules are valuable for a basic study of the water molecules transport across the air/solution interface. In this study, using UV–VIS reflectometry and Attenuated Total Reflection (ATR) in infrared region, the water evaporation from layers of such aqueous solutions has been investigated. Physical processes as water evaporation and diffusion of water molecules between the glycols' molecules have been revealed. The UV–VIS reflectometry method investigated the evolution in time of the layer thickness due to evaporation, while the ATR-IR method monitored the compositional changes, too. A comparative study of the results obtained via these two measurement methods is made.

1. Introduction

Within a water molecule the oxygen and hydrogen atoms are bounded via covalent bonds, sharing one or more pairs of valence electrons. This distribution of the electrons around the three atoms determines an electrical dipole associated to the water molecule, with the centrum of negative charge placed in the region of the oxygen atom. A multitude of water molecules means an equal number of electrical dipoles that interact between them. A special case of interaction is the attractive force between the hydrogen attached to a water molecule and an electronegative atom (oxygen, in the case of water molecules) of a different molecule: this is the *hydrogen bond* (*HB*). A water molecule can develop four HBs with four adjacent water molecules. Thermal motions cause individual HBs to break and re-form in new configurations in a 10^{-12}–10^{-9} s time scale [1]. These events at super-small time scale, determine most of the physical properties of water as a material.

When water is mixed with liquids from glycol family, HBs can be formed between these two types of molecules. Considering the ethylene glycol (EG) molecule, there are two oxygen atoms (for each of them being possible two HBs) and 6 hydrogen atoms (each being promoter for one HB [2]). But, not all hydrogen and oxygen atoms that could be partners in one HB will participate at such interaction because of the geometry of the glycol molecular structure. Also, one can anticipate differences between the HBs in the water–water molecule interaction and water–glycol molecule interaction. Padró et al. [3] have made a computer simulation study on the HBs between water and glycols as EG, tetraethylene glycol (TEG) and glycerol (GLY) and they found:

a) for EG and GLY, the largest part of the oxygen atoms have two HBs;
b) these two-HB oxygen atoms should be associated with branching (the EG and GLY structure is not linear);
c) the percentage of EG molecules with two HBs is low and even smaller than that in the case of GLY.

The properties of these associated liquids are largely determined by the number and the strength of their HBs. Solutions of water–glycols are used in many industrial (e.g. water-based paint [4], antifreeze, detergents) and domestic applications (e.g. pharmaceutical and cosmetic products [5]). The evaporation of water from these mixtures determines their functionality. There are applications where water–glycol mixtures are supposed to evaporate under different environmental conditions (temperature (T), relative humidity (rh), etc). A water molecule evaporates when all four HBs are broken and the molecule leaves the liquid surface. The strength of water–water HB is smaller than the water–glycol HB. The number of the HBs and their strength influence the diffusion rate of water molecules in such a mixture, and from here the evaporation rate (ER). Molecular dynamics simulations have been used to determine the evaporation rate of a thin water layer in normal conditions [6] and into vacuum [7]. The simulations show that the hydrogen bond has a significant effect on the molecular behavior near the liquid–air interface. Experimentally the evaporation rate was studied for various water-based liquid systems as: water-in-oil microemulsions [8], water–surfactant mixtures [9], ionic aqueous solutions (KCl) [10], water–glycerol

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http://dx.doi.org/10.1016/j.tsf.2012.11.114

solutions [11], etc. In most of the published situations, the HBs are used to explain the processes related to water evaporation.

The compositional and structural changes in the O–H interactions (they could be HB-like or covalent) can be investigated with optical spectroscopy techniques. The UV–VIS reflectometry can be used to follow the water evaporation process in time; the IR Attenuated Total Reflection (ATR) technique reveals the phononic spectrum and its time evolution when water evaporates. Both techniques have been used in this study which aims to investigate the evaporation of water from water–glycol mixtures.

2. Experimental details

Mixtures of water with various glycols (EG, TEG and GLY) in different compositions (0%, 24%, 49% and 74% of glycol in water) have been investigated considering the process of water evaporation and adjacent phenomena (e.g. diffusion, hydrogen bonding). The evaporation rates have been calculated from UV–VIS reflectometry and ATR-IR spectra recorded in time with a certain periodicity. In order to confer a low surface tension to the liquid, 2% of surfactant has been added.

2.1. UV–VIS reflectometry method

The advantage of the optical interference phenomena is employed to determine the thickness of a liquid thin film within a special sample holder made on c-Si surface. The sample holder dimensions are: surface 25×25 mm^2 and depth 4 or 7 μm. Applying one UV–VIS beam under a very small angle of incidence to the liquid surface, the resulted reflectance spectra contain fringes of interference. The reflection spectrum is recorded by an Ocean-Optics spectrometer with a controllable periodicity. The Scout program [12] is used to simulate the measured spectra and it outputs the thickness of the liquid layer.

2.2. IR-ATR spectroscopy technique

The IR-ATR measurements have been made with a Bruker Vertex 70 FT-IR spectrometer covering the wave-number range of 600–4000 cm^{-1} with a resolution of 4 cm^{-1}. This system is equipped with a MCT detector cooled with liquid nitrogen; the DigiTect technology implemented provides a high signal-to-noise ratio. All measurements have been made at room temperature.

An IR radiation is sent on the ATR crystal, which is the bottom of the sample holder. The angle of incidence and the refractive index of the investigated liquid and of the crystal (Ge in this case) will determine the depth of penetration, δ_p, for the evanescent wave assigned to the crystal/liquid interface. When the thickness, d, of the liquid from the sample holder is bigger than δ_p, the ATR spectra gives information about the composition of the liquid. A special model for data analyzing has been prepared. The sample-holder with a surface of 4 cm^2 can host a liquid layer of 1 mm. The basics of the theoretical background for ATR measurements can be found in Harrick's book on internal reflection spectroscopy [13].

3. Results

3.1. UV–VIS reflectometry

The output of a reflectometry measurement is the reflectance spectrum and a typical example is shown in Fig. 1 for a sample formed from 74%H_2O and 24%EG. Similar spectra are measured with a periodicity of 1 s. The Scout simulation is in dotted line. In order to qualitatively reveal the evaporation process, the color-scale plot has been chosen: the reflectance level is given by the color scale while the Oy axis gives the moment of spectrum measurement. Fig. 2 shows such an example. The water evaporation decreases the liquid thickness and this is revealed in time by the inter-fringe distance that increases. Also, the fringes' maxima shift towards the low wavelength values.

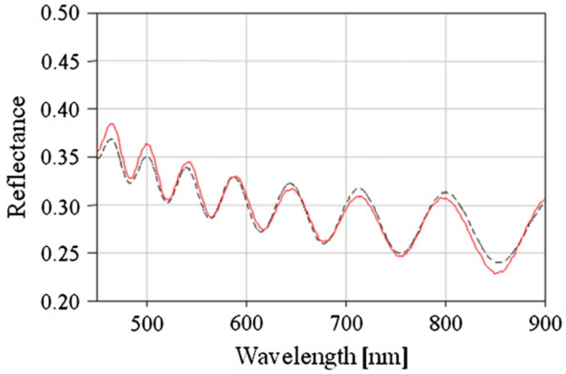

Fig. 1. The measured reflection spectrum (continue line) and the Scout simulated spectrum (dottedline) for the 74%$H_2O + 24\%$EG sample.

Using the technique of spectrum simulation, the layer thickness is calculated for each measured spectrum. The evaporation rate is easily determined plotting this thickness against time. Such data for the 74%$H_2O + 24\%$EG sample are shown in Fig. 3, and two evaporation regimes are revealed: one with a constant rate (the layer thickness linearly decreases in time) and the other one with a decreasing evaporation rate (more about this in the next section). The constant evaporation rate for this sample is 65.8 nm/s.

3.2. IR-ATR spectroscopy

The method of ATR is used to identify molecular species and to calculate the material composition. It has to be mentioned that the probed sample is limited at the penetration depth of the IR beam into the liquid on the ATR crystal. A typical ATR spectrum of a mixture $H_2O + EG +$ surfactant is shown in Fig. 4. The peaks assigned to the main components, according to their position (cm^{-1}), are: H_2O_1637, H_2O_3350, EG_1042 and EG_1085 [14]. The band situated between 3000 cm^{-1} and 3600 cm^{-1} is complex and contains the spectroscopic response of different OH groups from the mixture.

The continuous-line spectrum is that of the initial state of the liquid mixture, with water content according to the initial composition. The evaporation of the water at the layer surface induces compositional changes via water diffusion from the bottom towards the liquid free surface. This change is revealed by the next spectra as it can be seen in Fig. 4: the peak assigned to water vibrations decreases in intensity, while that of EG increases because of composition rise. The dot-spectrum is the last

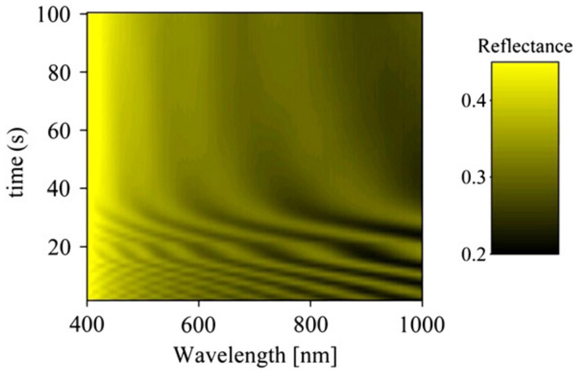

Fig. 2. Using the color-scale plot, various regimes in the water evaporation are revealed. After t = 34 s the layer thickness remains quasi-constant and the sample consists of EG with water molecules trapped by HBs.