Evaporation of binary mixtures and precision measurement by crystal resonator

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ABSTRACT

Theoretical and experimental investigations are presented for the precision measurement of evaporation kinetics of binary mixtures using a quartz crystal resonator. A thin layer of light alcohol mixture including a volatile (methanol) and a much less volatile (1-butanol) components is deployed on top of a crystal resonator for the evaporation experiment. A one-dimensional theoretical model is developed to describe the underlying mass transfer and interfacial transport phenomena. Along with the theoretical analysis, the transient evaporation kinetics, moving interface, and the stratification of viscosity of the liquid mixture during evaporation can be simultaneously measured by the impedance response of the shear and longitudinal waves emitted from the resonator. The result on the binary mixture presents a simplified model system for further investigations of complicated evaporation kinetics involving complex fluids or multi-component fuel systems.

1. Introduction

Quantitative analysis of evaporation kinetics of binary or multi-component fluid mixtures is important in many applications ranging from petroleum, transportation, pharmaceutical, to biotechnology industry. Properties of the multi-component fluids are determined by the composition and concentration of the base fluids. Their dynamic behaviors also depend on the transient evolution of the base fluids involved in the process. Thereby better understanding of evaporation kinetics is important in designing, controlling, and optimizing the relevant chemical processes. Evaporation of small liquid drops can be measured by atomic force microscope cantilevers [1] with high sensitivity and time resolution and with the surface tension effect taken into account. For a simpler experiment, it is known that quartz crystal microbalance (QCM) or resonator along with dissipation (QCM-D) and electrochemical (E-QCM) methods have been successfully applied to ultrasensitive mass detection, thin film thickness and rigidity detection, viscosity measurement, and sensing of various interfacial molecular activities, e.g. [2,3,5,4,6]. A few investigations have shown that evaporation kinetics of pure [7–9] and complex fluids

including suspensions [11,10] and polymer solutions [12] can also be measured by crystal resonators. However, theoretical modeling and data interpretation on multi-component systems are only at the beginning stage. The full potential of quartz crystal resonator as a low cost, repeatable, highly sensitive, multi-mode and in-situ sensor for characterizing simple and complex fluids is largely unexplored.

A thin film deposited on top of the surface of an oscillatory crystal will lead to a reduction of the resonant frequency of the whole system [13]. This is because the shear wave propagated into the film deposition increases the effective thickness of the crystal. Similarly, a sessile liquid droplet or liquid layer loaded on top of a crystal resonator will also lead to a change of frequency response [14]. For Newtonian fluids, Kanazawa and Gordon first developed a physics-based model to connect the frequency shift of the resonator to the fluid properties [15,16]. Their result has been broadly applied to viscosity measurement, which only requires a small amount (less than 1 mL) of liquid samples to perform the precision experiment. In addition to the oscillatory shear motion, crystal resonator also oscillates in the normal direction simultaneously and produces a longitudinal acoustic wave propagating toward the liquid–vapor interface [17]. The acoustic wave partially transmits and reflects at the liquid–vapor interface. The reflected wave again propagates through the liquid layer (Fig. 1) and causes resonance

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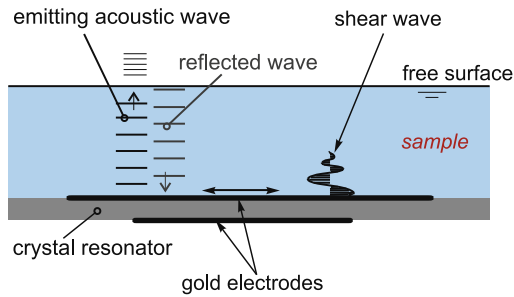   *E-mail address:* thfan@engr.uconn.edu (T.-H. Fan).

Fig. 1. Schematic showing a liquid layer deployed on top of a quartz crystal resonator, the shear wave near the crystal surface, the longitudinal acoustic wave that penetrates through the liquid layer and is partially reflected by the free surface. The resonator is made of piezoelectric material with electrodes coated on top and bottom surfaces.

Fig. 3. Schematic of the 1D evaporation of methanol–butanol mixture with assumed equal amount of methanol and 1-butanol initially. The spatial coordinate origin is located on top of the crystal surface. Time instances t_1 and t_2 indicate transient evolution of the concentration profiles, and δ is the thickness of the whole liquid layer, which also indicates the location of the free surface moving toward the crystal surface. J_M and J_B are diffusive fluxes of methanol and butanol, respectively. J_B in vapor phase is assumed negligible. The velocity v is for the uniform upward draft everywhere in the vapor phase.

in the liquid while the thickness of the liquid layer evolves to a multiple of half wave length [18]. Each resonance will create a spike response on the mechanical impedance to the crystal, essentially a jump of hydrodynamic resistance to the crystal's motion. Therefore, a transient evaporation on top of the resonator will generate a sequence of spikes (Fig. 2) that one can use to extract the time evolution of the moving liquid–vapor interface with spatial resolution down to several microns. The speed of the moving interface represents the mass flux and directly characterizes the evaporation kinetics (see Fig. 3).

Here we apply the crystal resonator at the megahertz frequency for the precision measurement of evaporation kinetics of binary (methanol and 1-butanol) fluids. These light, monohydric alcohols are selected as a simplified model system because of their distinct volatility and similar molecular structure for an ideal solution behavior. The evaporation kinetics is measured by the resonant pattern of the acoustic wave (Fig. 2), while the viscosity stratification in liquid mixtures during the evaporation process is evaluated by the shear wave near the surface. Fig. 2 shows a typical impedance response of the resonator in terms of the shift of the resonant frequency versus time, demonstrating that methanol evaporates much faster than 1-butanol, and as expected the evaporation rate of a mixture of methanol–butanol is in between pure methanol and pure butanol. Time evolution between spikes indicates a reduction of the thickness of the liquid layer by a half of acoustic wave length, around tens of microns. The resonant frequency shift along the base of the signal line is connected to the change of local density and viscosity of the mixture. By tracing

the impedance or frequency response and applying the multiphase modeling results, the evaporation kinetics and transient composition of the liquid layer can be resolved simultaneously.

From modeling perspective, an isothermal evaporation process driven by vapor diffusion from a free surface is categorized as the Stefan problem [19,20]. The analytical result for cases with stationary phase change interface was developed by Lee et al. [21] and later by Prata et al. [22]. Approximation of more complicated isothermal evaporation of a pure and ideal binary mixtures that involve a moving interface was first proposed by Slattery and Mhetar [23,24]. In their model for the binary mixture, the interface concentration is presumed fixed to facilitate the analytical solution. The diffusion-induced bulk flow was resolved by Chebbi and Selim [25]. A similar binary problem but with multiple gas components, in which the Stefan–Maxwell equation is applied to describe multi-component diffusion, was investigated by Carty and Schrodt [26]. An ideal binary mixtures may consist of a volatile and a nonvolatile liquids with or without density difference [27]. To facilitate the analytical approximation, a simplified boundary condition to define the concentration at the liquid–vapor interface is usually assumed. A more realistic interfacial condition for an ideal mixture is to take concentration partition into account based on the Raoult's law, i.e., a transient jump concentration across the interface. This interfacial condition plays an important role in characterizing evaporation kinetics of multi-component liquids. Here a one-dimensional numerical model and analytical approximations are developed to predict the concentration field, the change of local viscosity, the moving interface, and the evaporation kinetics of the mixture. The models connect the underlying mass and momentum transport principles to the experimentally observed impedance response for data interpretation.

2. Theoretical analysis

A few assumptions are proposed next to simplify the theoretical analysis. A thin layer of methanol–butanol liquid mixture is deployed on top of the crystal resonator. The bare crystal has resonant frequency about 5 MHz. The thickness of the liquid layer is around 1 to 4 mm, much less than the diameter of the crystal around 2.4 cm, and thus the one-dimensional approximation is appropriate for the problem in hand. Fig. 1 shows the schematic of the 1D model. Because the saturation pressure of methanol, ~16.9 kPa under ambient conditions [28], is much higher than that of the 1-butanol, ~0.9 kPa [29], here only methanol is considered volatile and exists in the gas phase such that the
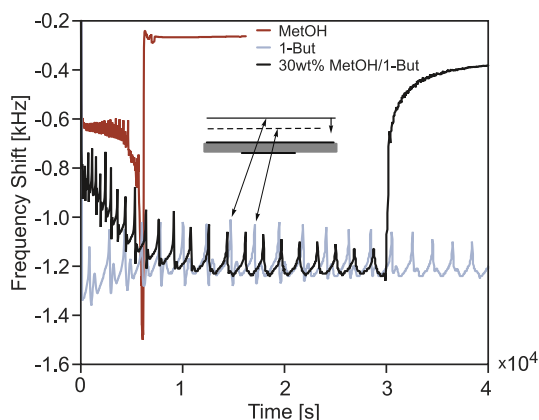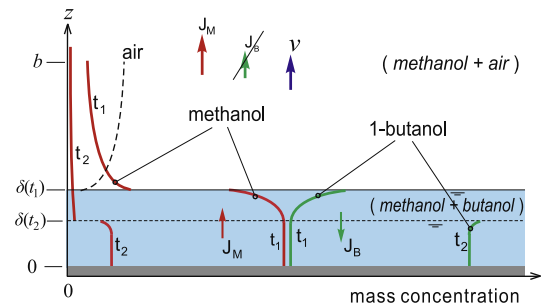

Fig. 2. A typical impedance response in terms of frequency shift of the resonator versus time during the evaporation process. Samples applied are pure methanol, pure 1-butanol, and methanol (30%)-butanol mixture. Figure inset indicates the free surface locations that correspond to two consecutive resonant spikes.