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Quartz crystal microbalance (QCM) as a rapid and cost-effective tool for solvent power studies in the paints and coating industry

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Abstract

Quartz Crystal Microbalance (QCM) is an extremely sensitive mass sensor that measures micro down to nanogram level changes in mass per unit area. The frequency of oscillation can be affected by the addition or removal of small amounts of mass onto the electrode surface. This change in frequency can be monitored in real-time to obtain useful information about molecular interactions or reactions taking place at the electrode surface.The QCM can provide useful information on the amount of mass deposited and the rate of deposition (or removal) of such films by monitoring the real-time change in frequency. In this paper, QCM is used as a cost-effective and efficient sensor to study the solubility of solvents used in the coating and paint industries. The results show that QCM can determine the volatility and solubility of a solvent, which are important parameters in choosing a solvent or multi-solvent system to achieve the best solubility and the most appropriate drying time of the paint. Therefore, this method can be used instead of the traditional and standard method of determining the number of Kauri, which is a time-consuming method that requires the use of n-butanol solvent.

Keywords: QCM sensors, solvent power, volatility, acetone

Introduction

The Quartz Crystal Microbalance (QCM) is an extremely sensitive, simple, cost-effective, and high-resolution mass sensing technique that allows a user to monitor small mass changes on the nanogram ranges on the surface of a coated quartz crystal. A QCM sensor typically consists of a thin AT-cut quartz disc with circular electrodes on both sides of the quartz. Due to the piezoelectric properties of the quartz material, a voltage between these electrodes leads to shear deformation of the quartz crystal. This leads to a connection between a mass deposition on the quartz surface and the resulting shift in the fundamental oscillation frequency of the quartz [1]. The researcher demonstrated the use of the quartz crystal microbalance (QCM) in solution For detection of electroactive cations using an electroactive polymer film attached to a quartz crystal microbalance. [2] The QCM functions as a mass-sensitive detector at the solid/solution interface. The researcher used the study of QCM for electrochemical phenomena. One of the applications of QCM redox chemistry is the use of the QCM to monitor the movement of ions in and out of electroactive polymer films. The frequency of the QCM reflects the mass of ions and any trapped solvent in a polymer affixed to the QCM surface [3]. In industrial and agricultural sources, because of undesirable smells spread, because of low cost, the potential of high integration they used gas sensors based on QCM. The response of the sensor in the exposure of gas involves the type and concentration, period of exposure [4]. We can get the QCM how quantitative data about the thickness, shear viscosity of the protein film. The QCM techniques because of the feature of sensitive and efficient tool for real-time measurement of macromolecule in several liquid-phases research applications such as electrochemistry (EQCM) and biotechnology to measure [5]. The function of a method is limited by the sensitivity of noise and the accuracy of the measurement. The important parameter of QCM is density and viscosity. And for SPR dielectric constant. QCM and SPR are both waves. Both represent resonance structures [6-7]. Some advantage and drawback of QCM are as follow [8]: Can be used as a sensor device without labeling, the frequency changes are proportional to the mass deposited on the electrode, Because of the high-frequency oscillation, it has high sensitivity, it has a simple construction, it has a low operation cost. Factors like air, humor, dust, etc cause to change in the crystal. The QCM device consists of a thin quartz plate with two electrodes on either side. Applying AC voltage across the crystal induces deformation in the crystal, and the sauerbrey equation is used to correlate the mass change with the frequency change in the QCM method. In this equation, Δf is frequency change; f0, resonate frequency; Δm, mass change; A, the area between electrode; ρ, the density of quartz; μ, shear modulus of quartz.

$$\Delta f = \frac{2f_0^2}{A\sqrt{\rho\mu}}\Delta m \qquad (1)$$

According to this equation, as the mass added to the quartz increases, the frequency will decrease. In order for the above equation to be used correctly, there must be conditions [9-10]: First, the mass is uniformly distributed throughout the crystal. Second, the mass deposited on the crystal must be hard and rigid. If the added layer is soft and thick or not fully coupled, the equation is not valid.

The Kb or Kauri-Butanol value is a test for the ability of a hydrocarbon solvent to overcome these binding forces in a standard solute. The Kb test is one of a number of "cloud-point" determinations that can be used to order solvents in a ranking based on relative solvent power. Other cloud-point determinations are aniline cloud-point, solubility grade, wax number, and heptane number. All have their specific uses, but Kb value is the most widely used test for gauging the relative solvent power of most hydrocarbon solvents.[11-12]

Kauri resin is a fossilized resin derived from the sap of the Kauri pine tree, which grows primarily in New Zealand. This resin dissolves easily in normal butyl alcohol (butanol) but will not dissolve very well in hydrocarbon solvents. To run the Kb, one dissolves 20 grams of the Kauri resin in a fixed amount of n-butanol. This solution is then titrated with the hydrocarbon solvent to a "cloud-point" or until the clear solution first turns slightly turbid or hazy. To make the cloud point easier to see, the test is usually performed over a page of ten-point type. When the ten-point type becomes slightly blurred or not quite crystal clear, you have reached the cloud point.

The volume or number of milliliters of hydrocarbon solvent used to reach the cloud-point is reported as the Kauri-Butanol or Kb Value of the hydrocarbon solvent. By this methodology, the greater the volume of solvent needed to reach the cloud point, the stronger the hydrocarbon solvent. A solvent with a Kb value of 100 (ml) is a much stronger solvent than one with a Kb value of 50.

In the paint and resin industry, measuring the solubility and volatility of solvents is important because different applications would have different requirements in terms of solubility and volatility of solvents. One common test to measure solubility is the kauri test. this test requires an expensive and rare resin called Kauri resin, which is used in all solvents and Lacquer to compare the solubility. QCM is cost-effective compared to the kauri test and it has proved that the more rapid the solvent evaporates, the more rapid the crystal frequency becomes stable and vice versa. This method can also test the solubility of a type of polymer with a special resin in different solvents.[13-14]

Experimental: According to Figure (1), the QCM circuit was fabricated in the laboratory and used to investigate solubility and volatility.Figure (1) shows schematics of the QCM.Figure (2) shows the experimental setup.

Figure (1) Schematics of the QCM circuit developed in the laboratory.

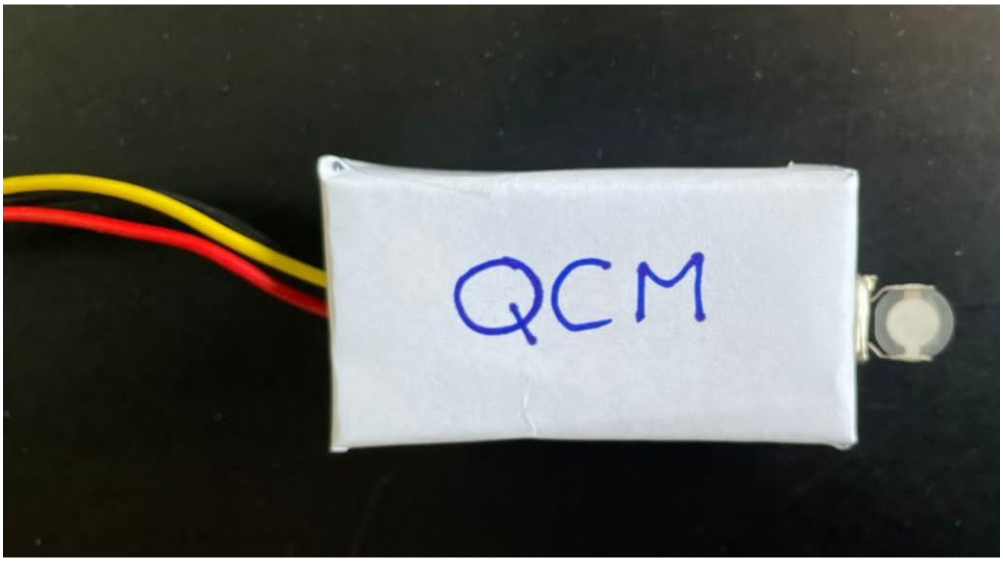

Figure (2) Quartz Crystal Microbalance set up.

The experiment section was performed in 4 steps as follow:

Firstly, the QCM performance was verified using the deposition of two consecutive droplets of 3.5% W/V solution of NaCl in water.NaCl is a non-volatile solid and when deposited on the quartz crystal surface, the frequency shift of the QCM can be monitored.

Secondly, two droplets of a solution of commercial nail lacquer in acetone were deposited one after another on the surface of the QCM crystal. Acetone as the solvent was allowed to evaporate and the frequency shift (increase in frequency) of the QCM was recorded versus time. It is obvious that more volatile and thereby less strong solvents reach faster to an equilibrium so resulting in a less time of frequency shift plateau.

Figures (3), (4) and (5), (6) show the time trend of the frequency shift of QCM for these two sets of experiments, respectively.

Results and Discussion

In the first experiment pure solution of NaCl was used. By injecting with a syringe, some of the solution to the surface of the crystal, every minute the changes of frequency are recorded. This process happened eight times.

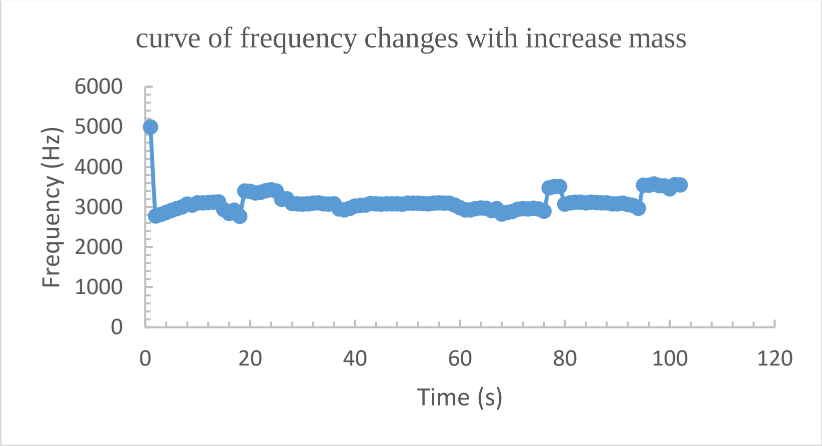

Figure (3) Frequency shift of QCM during the deposition of NaCl solution.

In the next series of experiments, the solution of NaCl is used again but injected with a syringe on the surface of the crystal.

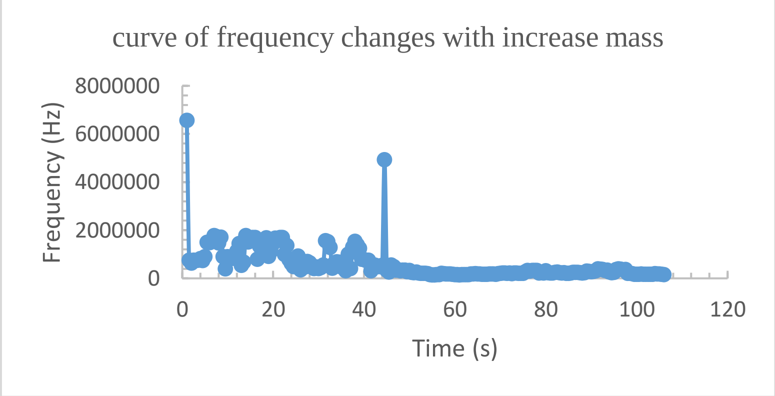

Figure (4) illustrates increase NaCl solution surface of crystal

Third experiment: Used Acetone organic solution. (The more volatile when the boiling point of organic solution is low.) First injected pure acetone, then every minute registered changes of frequency and added some Lac to acetone and solved it, injected to the surface of the crystal and registered the changes.

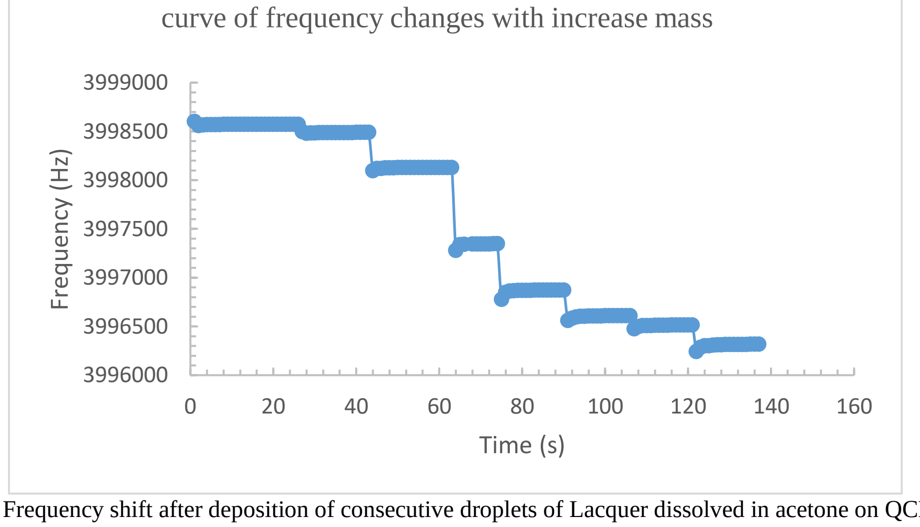

Figure (5) Frequency shift after deposition of consecutive droplets of Lacquer dissolved in acetone on QCM. crystal.

In the Fourth experiment : Used acetone + Lacquer

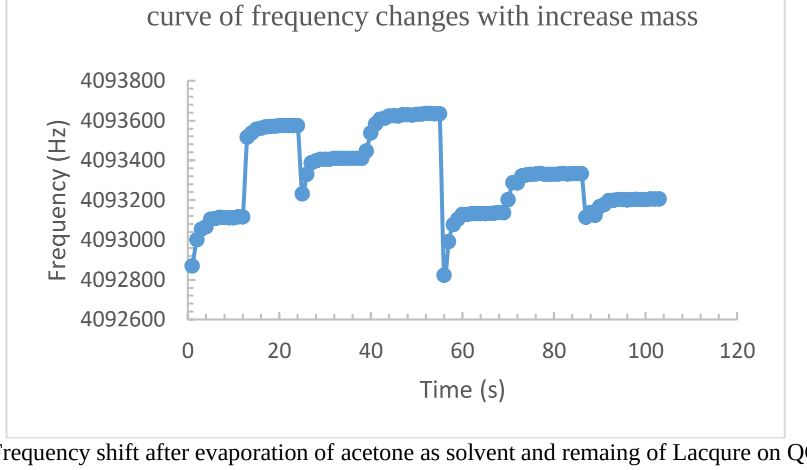

Figure (6) Frequency shift after evaporation of acetone as solvent and remaing of Lacqure on QCM crystal.

Conclusions

Observed results indicate that this method can be used to test the solubility and volatility of different types of polymers, resins, and different colors in different solvents.

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