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The Effect of KCL Solution Ionic Strength to QCM Sensor Response Coated with PVC-Polystyrene-Crown Ether

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Abstract. The interaction between the surface of the material and the ionic solution can cause many different effects on the material. One impact that might occur is material swelling. The swelling of the polymer in the form of thin films causes changes in the mechanical property of the materials. Swelling results in an expansion of the volume of the polymer. In turn, it changes molecular density, modulus of elasticity of the film, and penetration of solution to the polymer. When the polymer film is deposited on a Quartz Crystal Microbalance (QCM) sensor, the change in the mechanical affects the sensor's resonant frequency. This study shows ionic strength with an average effect of the concentration of potassium chloride on a polymer film mixed between polyvinyl chloride (PVC), polystyrene (PS), and the crown-ether (CE) associated with changes in the frequency of the coated sens[illegible] Minimum impedance measurements show that changes in the mechanical properties of the thin film are observed. The resonant frequency of the QCM sensor decrease with time when interacting with a potassium chloride solution. While the minimum impedance at series resonance remains constant. Distilled water and KCl solution, which is varied, are used to analyze the effects of swelling that occur. The result shows that the amount of the frequency decrease depends on the concentration of the KCl solution.

INTRODUCTION

Polymer membrane is a material that is used as a coating layer as well as a functional layer to detect an analyte. This membrane consists of a polymer matrix, membrane solvents (plasticizer), ionophores, and ionic additives [1]. For chemical sensor applications, this membrane usually consists of valinomycin as an ionophore. The ionophore is incorporated into polymers such as Poly Vinyl Chloride (PVC) without lipophilic ionic. In addition to valinomycin, organic crown ether compounds are used as compounds to increase the selectivity of polymer membranes [2]. This compound has a structure such as a valinomycin and shows selectivity to alkali metals and alkaline earth metal cations [3] in the solution phase [4]. The use of PVC polymers as a matrix of polymer membranes is because PVC has a superior surface property than other polymers [5–8].

Nonetheless, the surface of a PVC-based sensor has been reported to show membrane instability [9] and poor adhesion to semiconductor material [10]. The 18-crown-6-ether and polystyrene can be mixed with the PVC To overcome the instability and poor adhesion. The crown ether not only improves the stability of PVC membranes but also acts as a selective compound. The selectivity of the crown ether comes from its crown-like structure with a cavity diameter close to the diameter of potassium ions. Besides, these compounds also have a high affinity to potassium ions, so they tend to be more selective to potassium ions compared to other metal ions [4].

Detection of potassium ions using this polymer membrane occurs through a swelling effect mechanism. The swelling effect is an effect caused by the diffusion of molecules or ions from liquid injected on the surface of the PVC-PS-CE film. The swelling changes the mechanical property of the PVC-PS-CE. Besides, the diffusion of potassium ions increases the mass density. By understanding the swelling effect, the PVC-PS-CE can be used as one detection mechanism. The application of swelling effects for sensor applications has been widely used. The application ranged from an optical transducer [11] and the mechanical transducer [12,13].

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In this study, a PVC-PS-CE was coated on top of a Quartz Crystal Microbalance (QCM). The frequency and impedance spectrum change of the sensor was studied. The composition of the PVC-CE was varied whilst the PS remained. Liquid tested in the form of distilled water and KCl concentrations of 1M and 2M. The sensor resonance frequency is taken to determine the effect of variations in the composition of PVC-PS-CE on the swelling effect. The impedance data were taken to determine the effect of ionic liquid interaction with the crown ether compound expressed on the mechanical property change of the PVC-PS-CE film.

MATERIALS

The QCM sensor used is a QCM sensor with a silver electrode with a basic resonance frequency of 10 MHz. Polyvinyl Chloride used is PVC with a molecular weight of ~ 43,000, which was purchased from Sigma Aldrich. While the crown ether used is a type of 18-crown-6-ether with a molecular weight of 264.32 gr/mol purchased from the same company. The polystyrene used is a molecular weight of 192kD. The solvent used is Tetrahydrofuran (THF). The liquid injected is in the form of distilled water and KCL solution whose concentrations were varied from 1M to 2M. The composition of PVC/CE was varied in the ratio of 9:0, 9:1, 9:2, 9:3, and 9:4. The mass percentage of the polystyrene was fixed at 18% mass ratio to the PVC-CE mixture.

Making Thin PVC-PS-Crown Ether Coatings

PVC-PS-CE solution was made by mixing PVC, Crown ether, and polystyrene until it reaches a concentration of 4% for each solution composition in the THF solvent. The PVC-PS-CE film was deposited on the sensor surface by using a spin coating technique with a rotational speed of 3000 rpm for the 60s. The QCM sensor which has been coated with PVC-PS-CE was then left for 24 hours at room temperature to let the THF evaporated. The rest was the QCM sensor with a PVC-PS-CE film coating on its one surface. The other surface of the QCM sensor was coated using polystyrene by spin coating, as described elsewhere [14].

Measurement of frequency and impedance

The electrical impedance of a PVC-PS-CE-coated QCM sensor was measured using a Bode 100 from Omicronlab Vector Network Analyzer. While the frequency response of QCM sensors coated with PVC-PS-CE to three different types of liquid was measured using an in-house frequency counter system that has been calibrated to a rubidium oscillator. The frequency response of the QCM sensor was taken during 60 minutes of measurement of each liquid. The sensor's electrical impedance response was measured for 0 minutes, 20 minutes, 40 minutes, and 60 minutes.

RESULT AND DISCUSSION

Crown ether is an organic compound that has a structure such as a micelle crown ether with a cavity diameter of 260-320 pm, which can form a complex compound with several metal ions such as potassium ions. Potassium ion has a diameter of 266 pm. Crown ether binds not only metal ions but also neutral analytes such as water, through the non-covalent interaction of van der Waals forces and hydrogen bonds. Crown ether cavities are polar, and the electron pair of oxygen atoms lining the cavity provides an effective solvation effect for alkali metal ions. So the crown ether is effectively used as a functional material in the PVC-PS-CE membrane for the detection of potassium ions.

When the PVC-PS-CE film deposited as a thin film on a QCM sensor in contact with the potassium ions solution, two possible mechanisms occur. The first effect is the mass density change of the film caused by the potassium ion diffusion. Assuming the diffusion does not change other film's mechanical properties, the mass density change results in a resonance frequency change due to the mass deposition. The other possibility is the change of the mechanical property of the film because of the ionic strength of the potassium solution. This effect results in a change in the resonant frequency of the QCM sensor. Both of the effects result in a resonance frequency change of the QCM sensor in contact with the potassium solution.

The frequency change of the QCM sensor due to liquid contact is presented in Fig. 1. The resonance frequency of the QCM sensor in contact with air was taken as an initial frequency and plotted as zero. The resonance frequency change is presented up to 4000 seconds. The resonance frequency of the sensor changes quickly into around -8KHz as the sensor surface in contact with water or potassium chloride solution. In contact with water, the resonance frequency of the sensor remained in its value. It can be assumed that not all molecules in water can diffuse into the PVC-PS-layer. So the graph decreases in frequency tend to be constant over time.

As the sensor surface in contact with the potassium chloride solution, the resonance frequency of the sensor changes. The resonance frequency of the sensor continuously decreased with time. The resonance frequency change of the sensor was increased with the potassium chloride solution concentration. The frequency change in contact with 2M KCl is bigger than the 1M KCl. It can be assumed that the film adsorbs and absorb potassium chloride molecules or ions. The resonance frequency decreased continuously. We assumed that the continuous decreased of the resonance frequency caused by the ionic strength of the solution. The ionic strength of the solution causes PVC-PS-CE swelling. As the film swelled, the potassium chloride ions, as well as the water, can penetrate into the film. The mechanical property of the film and the mass density of the film with absorbed potassium chloride solution changed. This leads to the frequency change of the sensor. This change in resonance frequency in Fig. 1 indicates a change in the mechanical property of the thin layer of hydrogel superimposed on the surface of the QCM sensor due to the appropriate absorption of solvents [15]. This frequency is also affected by the ionic strength of the potassium chloride liquid. The greater the concentration of the electrolyte solution, the greater the ionic strength liquid, results in bigger frequency change.

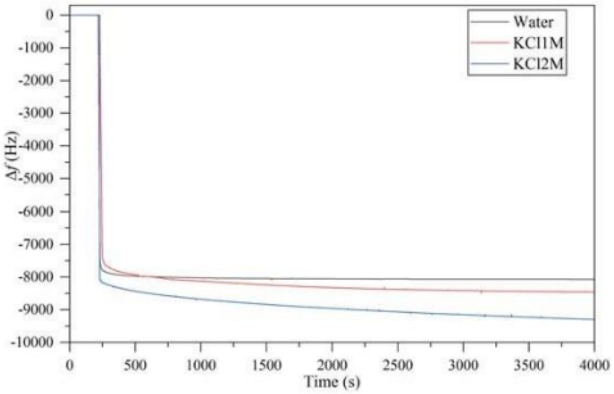

FIGURE 1. Changes in frequency with time in the layer of PVC / CE 9: 4

Variation in the composition of PVC / CE influences the sensor's frequency response change in contact with water and a monovalent KCl electrolyte solution. The crown ether is a polar group; therefore, the presence of the crown ether creates the PVC-PS-CE coating becomes hydrophilic. The attraction between the PVC-PS-CE layer and the KCl and water solution makes these molecules entering the layer. Fig. 2 shows the resonance frequency change of the sensor in contact with water and KCL solution after 3600 seconds from the first contact with liquid.

The frequency change of the sensor in contact with the KCl solution is bigger compare with the water. The origin could be related to the existence of the crown ether. The crown ether compound tends to interact with potassium ions from the KCl solution and trap the potassium ion in its cavity. In addition, the KCl solution also has ionic strength, which helps the molecules more easily enter the PVC-PS-CE layer. The bigger the concentration of KCl solution, the bigger the frequency change. Besides, an increase in the composition of PVC / CE also affects a decrease in frequency. The greater the composition of PVC / CE, the greater the decrease in frequency. This is due to an increase in ether groups and hydrogen bonds in the layer so that more ions or molecules interact with the layer.

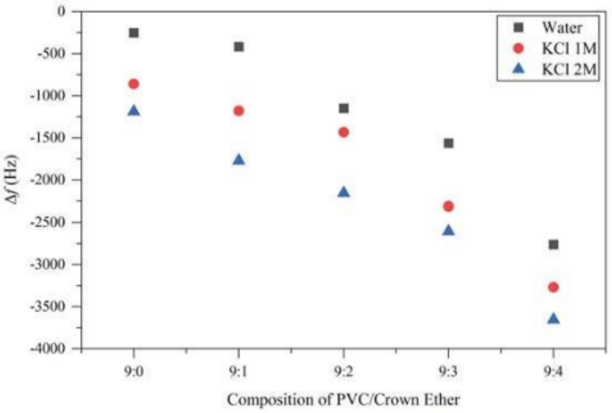

FIGURE 2. Changes in frequency to the composition of the PVC layer / Crown Ether

Based on the gravimetric response of the QCM sensor using the Sauerbrey equation [16], the film thickness and potassium chloride mass deposition on the film can be calculated. Taken by an assumption of glassy film and smooth surface, the film thickness calculated using the Sauerbrey equation is 283nm. The total mass KCl solution for each injection (40 μL) gives a total mass of the KCl in the sensor chamber of 0.3 μg and 0.6 μg, respectively, for 1M and 2M solution.

Table 1 lists the calculated deposited mass of potassium chloride based on the gravimetric effect assumption. The calculation was taken, assuming that the film was glassy and its mechanical property stills. It can be seen that the calculated deposited mass based on the frequency change of the QCM sensor differs among PVC-CE composition. Higher crown ether part results in bigger calculated mass. When the effect is purely mass deposition, the frequency shift should not change or little variation among different compositions for the same KCl concentration.

TABLE 1. Calculation of KCl mass absorbed in the PVC / CE layer using the Sauerbrey equation.

Composition	Δf of KCl 1M (Hz)	Calculated Mass of KCl 1M (μgram)	Δf of KCl 2M (Hz)	Calculated Mass of KCl 2M (μgram)
9:0	-860	0.75	-1188	1.03
9:1	-1179	1.03	-1771	1.54
9:2	-1433	1.25	-2157	1.88
9:3	-2312	2.01	-2605	2.27
9:4	-3270	2.84	-3653	3.18

The measured frequency change of the QCM sensor with PVC-PS-CE in contact with KCl solution shows that the frequency change, as depicted in Table 1 was not only caused by solution absorption nor KCl ion deposition. Further analysis was done by measuring the minimum impedance of the sensor in contact with the KCl solution. Fig. 3 shows the minimum impedance of the QCM sensor in contact with water and KCl solution with time and different PVC-CE composition.

The QCM minimum impedance of the sensor coated only with PVC-PS, without crown ether, shows the smallest impedance value compare with the other sensor coated with PVC-PS-CE. The crown ether plays an important role in the impedance increase because of its polarity, which makes the sensor surface more hydrophilic. The fraction of the crown ether, however, not significantly affect the liquid to sensor surface interaction. Even though the crown ether composition was increased four times, the minimum impedance of the sensor in contact with the solution was not changed significantly. Increasing potassium chloride concentration did not change the minimum impedance of the sensor for all of the sensors with different coating material compositions. The minimum impedance of the sensor after 60 minutes did not change significantly. It means that the mechanical property, by means of modulus elasticity, of the coating layer remains.

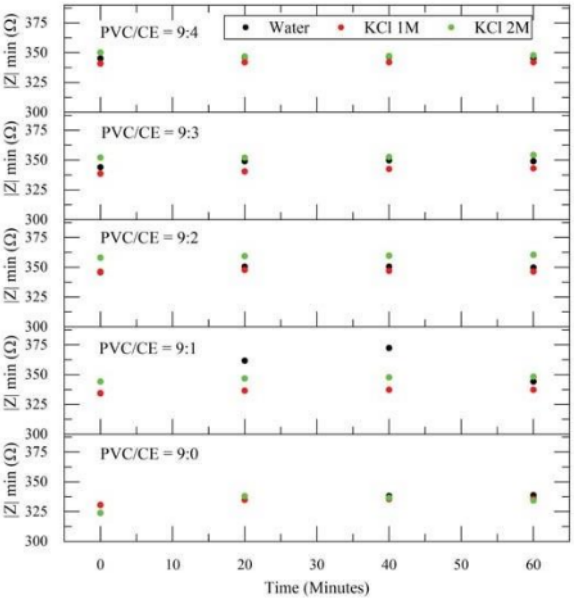

FIGURE 3. The minimum impedance of the QCM sensor in contact with water and KCl solution

By considering the observed data in Figures 1 to 3 and Table 1, it is predicted that the significant frequency change of the QCM sensor in contact with the KCl solution is attributed to other interactions between the film and the solution. As there is no observed change in the minimum impedance, but the frequency change was bigger than calculated ones based on the gravimetric calculation, the possibility is a higher absorption of the solution in the film. As the film swell, more solution penetrates into the film and contributes to an increased surface mass density of the material on top of the sensor.

CONCLUSION

This paper shows the effect of KCl solution concentration on the frequency response and impedance of QCM sensors coated with PVC-PS-CE film. The concentration of KCl solution is related to the ionic strength of the solution. The higher the concentration of KCl solution and the composition of crown ether results in a more significant decrease in the sensor's resonance frequency. The minimum impedance of the sensor was not affected by the KCl concentration nor the crown ether composition. It means that the mechanical property, by means of the modulus elasticity of the film in contact with the KCl solution, remains constant. Continuous frequency change of the sensor resonance could be attributed to the swelling of the film.

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REFERENCES

[1] Faridbod F, Ganjali M, Dinarvand R, Norouzi P and Riahi S 2008 Schiff's Bases and Crown Ethers as Supramolecular Sensing Materials in the Construction of Potentiometric Membrane Sensors *Sensors* **8** 1645–703

[2] Drake P L and Price G J 2000 Crown-ether containing copolymers as selective membranes for quartz crystal microbalance chemical sensors *Polym. Int.* **49** 926–30

[3] Pedersen C J 1967 Cyclic Polyethers and Their Complexes *J. Am. Chem. Soc* **2** 209

[4] Choi C M, Heo J and Kim N J 2012 Binding selectivity of dibenzo-18-crown-6 for alkali metal cations in aqueous solution: A density functional theory study using a continuum solvation model *Chem. Cent. J.* **6** 1

[5] Brennecke D, Duarte B, Paiva F, Caçador I and Canning-Clode J 2016 Microplastics as vector for heavy metal contamination from the marine environment *Estuar. Coast. Shelf Sci.* **178** 189–95

[6] Holmes L A, Turner A and Thompson R C 2014 Interactions between trace metals and plastic production pellets under estuarine conditions *Mar. Chem.* **167** 25–32

[7] Rochman C M, Hentschel B T and Teh S J 2014 Long-Term Sorption of Metals Is Similar among Plastic Types: Implications for Plastic Debris in Aquatic Environments ed J P Meador *PLoS One* **9** e85433

[8] Sin M C, Tan I K P, Annuar M S M and Gan S N 2014 Viscoelastic, Spectroscopic, and Microscopic Characterization of Novel Bio-Based Plasticized Poly(vinyl chloride) Compound *Int. J. Polym. Sci.* **2014** 1–10

[9] Mir M, Lugo R, Tahirbegi I and Samitier J 2014 Miniaturizable Ion-Selective Arrays Based on Highly Stable Polymer Membranes for Biomedical Applications *Sensors* **14** 11844–54

[10] Mikhelson K N 1994 Ion-selective electrodes in PVC matrix *Sensors Actuators B Chem.* **18** 31–7

[11] Oktar O, Caglar P and Seitz W R 2005 Chemical modulation of thermosensitive poly(N-isopropylacrylamide) microsphere swelling: a new strategy for chemical sensing *Sensors Actuators B Chem.* **104** 179–85

[12] Bashir R, Hilt J Z, Elibol O, Gupta A and Peppas N A 2002 Micromechanical cantilever as an ultrasensitive pH microsensor *Appl. Phys. Lett.* **81** 3091–3

[13] Carrascosa L G, Moreno M, Álvarez M and Lechuga L M 2006 Nanomechanical biosensors: a new sensing tool *TrAC Trends Anal. Chem.* **25** 196–206

[14] Sakti S P, Amaliya L, Khusnah N F and Masruroh M 2017 Effect of UV Radiation Duration and Molecular Weight to Hydrophobicity and Surface Roughness of Polystyrene Coating on QCM Sensor *J. Teknol.* **79** 61–7

[15] Richter A, Bund A, Keller M and Arndt K-F 2004 Characterization of a microgravimetric sensor based on pH sensitive hydrogels *Sensors Actuators B Chem.* **99** 579–85

[16] Sauerbrey G 1959 Verwendung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung *Zeitschrift für Phys.* **155** 206–22

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