Electrochemical reduction of vinyl chloride on a Au/porous alumina plate/Pt electrode assembly in nonaqueous electrolytes: Toward the development of gas sensors

M-C. CHUANG and M-C. YANG*

Department of Chemical Engineering, National Cheng Kung University, Tainan 70101, Taiwan
(*author for correspondence, fax: +886 6 234 4496, e-mail: mcyang@mail.ncku.edu.tw*)

Abstract

A novel configuration consisting of one porous alumina plate, two electrodes sputtered on both sides and an organic electrolyte, was developed to analyse *in situ* vinyl chloride in the gaseous phase. Gold and platinum with several solvents (e.g., 1,4-dioxane aqueous solution, acetonitrile and toluene/DMF mixtures) were applied to investigate the suitability for the analysis of vinyl chloride gas in the concentration range of 13–44.5%. The effect of solvent composition on the response behavior was discussed. The analyser with 20% toluene/80% DMF (v/v) mixture had the largest sensitivity at -2.3 V vs Ag/Ag$^+$. The content of residual water in the electrolyte affected not only the background current but also the reduction current of vinyl chloride.

1. Introduction

Polyvinyl chloride (PVC) is one of the most important plastic materials, in spite of some environmental concerns over its production process. It was expected that the total global production capacity of vinyl chloride monomer (VCM) would reach 33.01 million tons in 2003 [1]. Detectors would be necessary to determine the concentration of vinyl chloride gas in the pipelines and around the processing locations with valves, flanges and other components.

Gas chromatography (GC) is one selective and sensitive method for routine determination of organic compounds [2]. However, the use of GC for the routine monitoring of organic compounds is limited due to its complexity, high power dissipation, low portability and high installation and operation costs. These drawbacks prohibit the application of gas chromatography for the continuous monitoring in factories. Therefore, a variety of analytical techniques have been developed to solve these problems. Electrochemical methods for concentration determination of electroactive species at room temperature have been widely used. Many three-electrode electrochemical cells have been applied to analyse the concentration of organic compounds and to investigate the mechanism of organic electrochemical reactions in a number of previous studies [3–6]. Several solvents, such as dimethylformamide (DMF), acetonitrile, and dimethylsulfoxide (DMSO), and supporting electrolytes, such as tetraalkyl ammonium salts, have

been applied to study the electrochemical oxidation and reduction of organic compounds in liquid phase. The effect of the medium composition on the reaction current of neutral and charged electroactive species has been reported [6].

As for organic compounds in the gaseous phase, several kinds of assembly with metal electrodes on solid polymer electrolytes (SPE) have been developed to analyse the concentrations of organic reducing gases, such as alcohol vapour [7], ethylene [8], acetylene [9, 10], and formaldehyde [11]. Nevertheless, the assemblies were generally not very suitable to analyse oxidative organic compounds at very negative potential, such as chlorinated hydrocarbons. The reduction reaction of these species required such high overpotential which also resulted in the simultaneous electrolysis of water. The cathodic current for electroactive species was difficult to obtain due to the accompanying large current from water electrolysis. This problem could be solved with nonaqueous electrolytes which are difficult to reduce and sufficiently stable in the electrochemical reactions. Compared with the aqueous electrolyte, nonaqueous electrolyte provides higher solubility and a wider applicable potential range for the oxidative electroactive organic compounds. Traditional solid polymer electrolytes (e.g., Nafion®) are commonly used in aqueous medium, but are not suitable in nonaqueous medium. Therefore, PTFE films were used to separate the organic electrolyte from the electroactive gas in CO_2/O_2 [12] and methane [13] gas sensors. In the present

study, the solid polymer electrolyte was replaced by a porous alumina plate, which permitted the penetration of electrolyte from the electrolyte chamber to the surface of the working electrode and provided three-phase reacting sites for electrochemical reductions of gaseous vinyl chloride. Effects of electrode material and solvent compositions on the analytical behaviour of vinyl chloride were investigated.

Our long-term objective is to develop an electrochemical method (configuration) to determine gaseous oxidative organic compounds, such as vinyl chloride. As a result, a detector has been developed to monitor vinyl chloride gas in the concentration range of 0.5–4% [14].

2. Experimental details

The analytical system, as shown in Figure 1, consisted of a porous alumina plate (A) with two film electrodes (B&C) on both the sides, a reference electrode (F), and two chambers filled with electrolyte (E) and testing gas (G). To prepare the gas with a desired concentration, 99.9% vinyl chloride gas was first blended with highly pure nitrogen in a dilution setup, and then passed into the gas chamber (G). The gas flow rate was 170 ml min^{-1}. Before venting, the outlet gas from the gas chamber passed through the absorption columns of solvent and activated carbon. Either gold or platinum film was sputtered on both the sides of the porous alumina plate as the working and counter electrodes at 0.1 mbar vacuum by an Au ion sputter (JFC-1100, Jeol) or a Pt ion sputter (E-100, Hitachi). The sputtering conditions were 5 mA d.c. for 10 min and 20 mA d.c. for 3 min for the gold and platinum films, respectively. The thicknesses of Au and Pt films were estimated to be around 60 and 65 nm, respectively. The electrodes had the same geometric area of 3.14 cm^2. One shadow mask was used to form the electrode pattern. Silver-coated leadwires, 0.3 mm in diameter, were connected to working and counter electrodes with Ag paste. The reference electrode was a silver/silver ion electrode in an
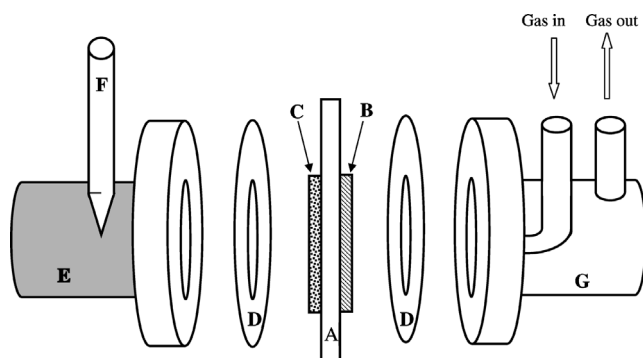
acetonitrile solution containing 0.01 M AgNO$_3$ and 0.1 M tetrabutylammonium perchlorate (TBAP). All the reported potentials were referred to the reference electrode. In the cell, the working electrode faced the testing gas on one side and the counter electrode faced the electrolyte on the other side. Two gaskets (D) were used to prevent the leakage of testing gas and electrolyte from two chambers.

A potentiostat (273A, EG&G) provided fixed potentials in chronoamperometric experiments to discriminate the current responses with and without vinyl chloride. The response current was calculated by subtracting the background current from the measured current. Flow controllers (Aalborg) were used to control the flow rate and concentration of VCM/N$_2$ gas. The water content in the electrolyte was measured with a moisture meter (CA-06, Mitsubishi).

The solvents of toluene (Tedia, 99.9%), N,N-dimethylformamide (Tedia, 99.9%), 1,4-dioxane (Tedia, 99.9%), and acetonitrile (Mallinckrodt, 99.7%) were used without further purification in advance. The supporting electrolyte, tetra-n-butylammonium perchlorate (TBAP), was purchased from Tokyo Kasei Kogyo Co. VCM gas was provided by Formosa Plastics Co. (Taiwan). The pore volume of the porous alumina plate (Leatec Fine Ceramics Co., Taiwan) was determined by nitrogen adsorption at 77 K with an automated adsorption apparatus (ASAP 2010, Micromeritiecs). The porosity and thickness of the porous alumina plate were 0.34% and 0.63 mm, respectively.

3. Results

3.1. *1,4-Dioxane aqueous electrolyte*

In the previous report [3], 75% dioxane/25% water mixture was used as an electrolyte to study the reduction behaviour of vinyl bromide. In this study, 75% dioxane/25% water mixture containing 10^{-3} M TBAP was used as the electrolyte to analyse gaseous vinyl chloride. Figure 2 shows the chronoamperometric curves recorded when the test gas changed from pure N$_2$ to 13% vinyl chloride at various applied potentials on platinum electrode. The responding currents were 2.2, 4.5, and 9.0 μA for potentials at −1.2, −1.6 and −2.0 V vs Ag/Ag$^+$, respectively. The responding currents were only 7–9% of their own background currents.

3.2. *Acetonitrile electrolyte*

Platinum electrode. Figure 3 shows the polarization curves of platinum electrode for 13% vinyl chloride with acetonitrile medium as electrolyte. The responding current had a maximum at the applied potential of −2.0 V vs Ag/Ag$^+$. When the applied potential was more negative than −2.0 V vs Ag/Ag$^+$, there occurred a large background current due to electrolyte reduction. The responding current with acetonitrile electrolyte was

Fig. 1. Schematic diagram of gaseous analytical system. Key: (A) porous alumina plate, (B) working electrode, (C) counter electrode (Pt), (D) gasket, (E) electrolyte chamber, (F) reference electrode (Ag/Ag$^+$) and (G) gas chamber.
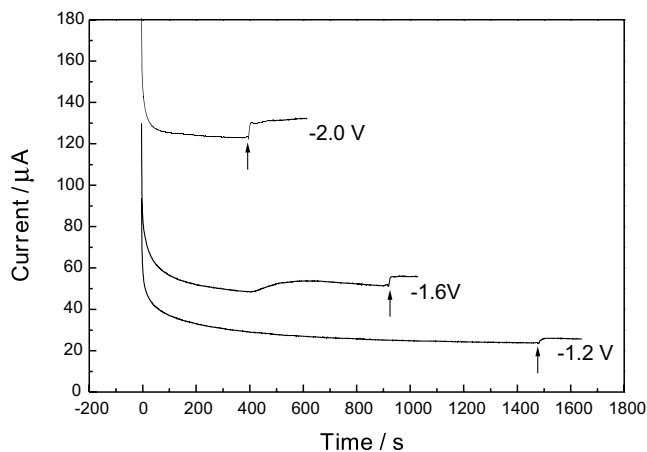
Fig. 2. Responding currents on Pt/porous alumina plate/Pt assembly at various applied potentials for 13% VCM gas in 75% dioxane/25% water mixture. Arrows indicate the starting times of 13% VCM exposure. Supporting electrolyte 10^{-3} M Bu$_4$NClO$_4$.
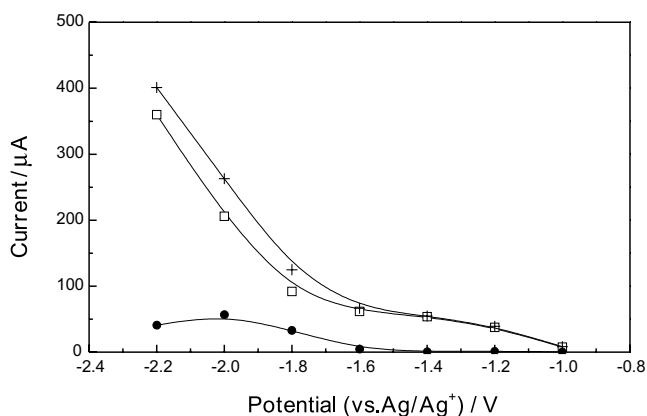

Fig. 4. I/E relationships for 13% VCM gas on Au/porous alumina plate/Pt assembly in acetonitrile. Supporting electrolyte 0.01 M Bu$_4$NClO$_4$. Key: (□) background current, (+) measured current, and (●) responding current.

Fig. 3. I/E relationships for 13% VCM gas on Pt/porous alumina plate/Pt assembly in acetonitrile. Supporting electrolyte 0.01 M Bu$_4$NClO$_4$. Key: (□) background current, (+) measured current, and (●) responding current.

Fig. 5. Response curve on Au/porous alumina plate/Pt assembly under increasing VCM concentrations in acetonitrile. Concentration of VCM changed from 0 to 13% and then increased with 10.5% interval. Supporting electrolyte 0.01 M Bu$_4$NClO$_4$, applied potential -2.0 V vs Ag/Ag$^+$.

6.4 times as large as that with dioxane aqueous electrolyte at the applied potential of -2.0 V vs Ag/Ag$^+$.

Gold electrode. By using the acetonitrile medium containing 0.01 M TBAP, the polarization curves of gold electrode for 13% VCM gas are as shown in Figure 4. The responding current maintained at 35 μA in the range -2.0 to -2.3 V vs Ag/Ag$^+$, and decreased when the applied potential became more negative than -2.3 V vs Ag/Ag$^+$. It was believed that the electrochemical reduction of the electrolyte occurred at potentials more negative than -2.3 V vs Ag/Ag$^+$ greatly and interfered with the reduction of vinyl chloride. Compared with platinum electrode in Figure 3, gold electrode gave larger responding current with smaller background current. The ratio of responding current to background current at -2.0 V vs Ag/Ag$^+$ was 0.465, which is larger than 0.276 on the platinum electrode. A significant increase in the electrolyte reduction on gold occurred at the potential of -2.3 V vs Ag/Ag$^+$, which is more negative than that on platinum electrode by 0.3 V.
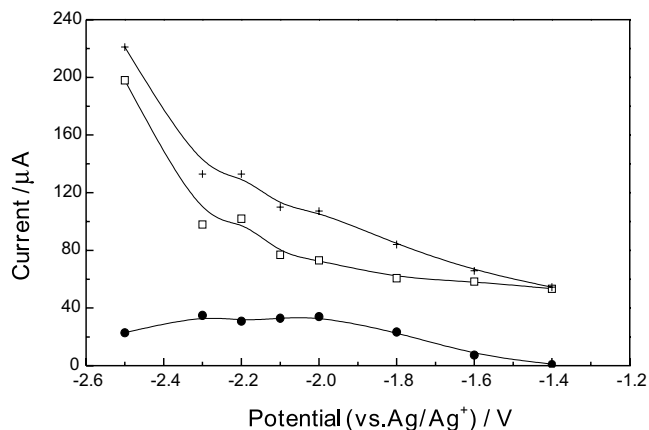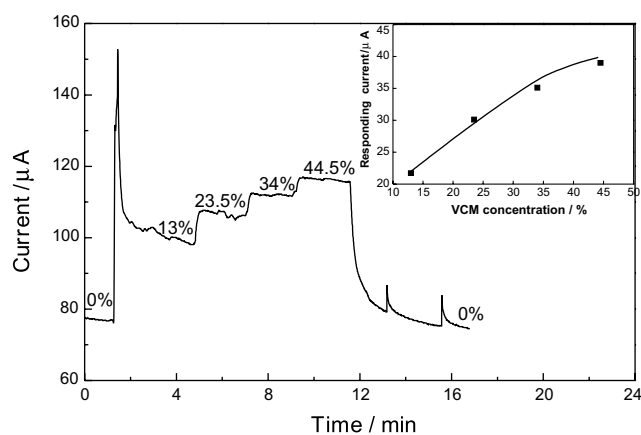
The chronoamperometric curve at -2.0 V vs Ag/Ag$^+$ for 0–44.5% vinyl chloride at a concentration increment of 10.5% is shown in Figure 5. Obviously, the measured current increased with concentration and finally recovered to the background current upon changing the gas to pure nitrogen. The insert in Figure 5 illustrates a linear relationship between the responding current and vinyl chloride concentration in the concentration range of 0–34%. The slope, namely the sensitivity for vinyl chloride, in this concentration range was 0.63 μA %$^{-1}$. The responding current for 44.5% was, nevertheless, smaller than that extrapolated from the above linear relationship. This phenomenon implied a lower sensitivity at concentrations larger than 34%. The response time, the time to reach steady state current, for each concentration change was within 20 s except for the first change. The recovery time was about 5 min. The two interfering signals at 13.2 and 15.6 min are due to the noise from instrument.

3.3. *Toluene/DMF mixture electrolyte*

The polarization curves of Au electrode for 13% vinyl chloride gas with three compositions of toluene/DMF mixture are shown in Figure 6. For each composition, the maximum responding current occurred at the applied potential of −2.3 V vs Ag/Ag$^+$. The order of maximum responding current was 50%/50% > 20%/80% > 80%/20%. The volume ratio of 50%/50% had the largest maximum responding current, 100 μA at −2.3 V vs Ag/Ag$^+$, for 13% VCM gas. This electrolyte also gave the smallest background current; whereas the electrolyte with the ratio of 20%/80% gave the largest background current.

Curve (a) in Figure 7 shows the effect of solvent composition on the ratio of responding current/background current at −2.3 V vs Ag/Ag$^+$. The electrolyte containing 50% toluene had the largest current ratio of 1.61 due to high responding current and low back-
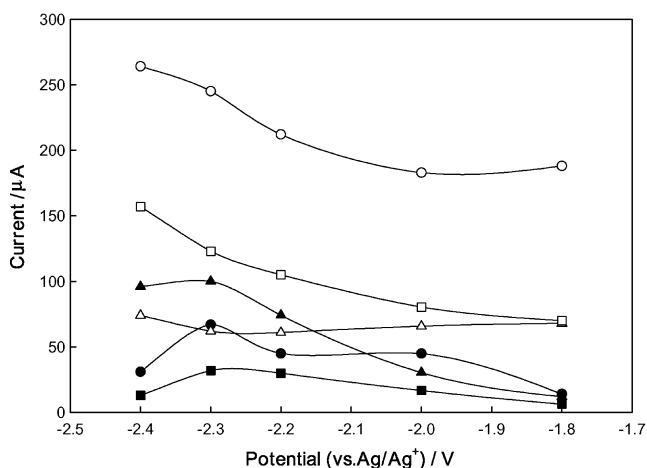

Fig. 8. Relationships between responding current and VCM concentration on Au/porous alumina plate/Pt assembly in toluene/DMF mixtures. Supporting electrolyte 0.01 M Bu$_4$NClO$_4$, applied potential: −2.3 V vs Ag/Ag$^+$. Toluene(%)/DMF(%): (■) 20/80; (●) 50/50; (▲) 80/20.

ground current. It was around 3.5, 6 and 6.4 times as large as those in acetonitrile, 20% toluene/80% DMF, and 80% toluene/20% DMF mixture, respectively. Although the electrolyte containing 20% toluene had smaller responding current and ratio of responding current/background current in 13% VCM than the electrolyte containing 50% toluene, the responding current in the former electrolyte was more dependent on the concentration of VCM gas (i.e., higher sensitivity). Figure 8 shows the relationships between responding current and concentration of vinyl chloride with the solvent mixtures of 20%/80%, 50%/50%, and 80%/20% at −2.3 V vs Ag/Ag$^+$ in the concentration range of 13–44.5%. Obviously, a straight section in the calibration curve was depicted for the concentration range of 13–34%, yet another section of the calibration curve with a smaller slope was used to fit the responding current obtained at the concentration larger than 34%. Our previous study showed that the sensitivity for vinyl chloride gas in the concentration range of 0.5–5% was observed as 5 μA %$^{-1}$ [14], and was around 2.3 times as large as that of 13–34%. This behaviour confirmed that different sensitivities for vinyl chloride existed in various concentration ranges. The curve (b) in Figure 7 shows that the sensitivity in the concentration range of 13–34% decreased from 3.42 to 0.57 μA %$^{-1}$ when the toluene content in the electrolyte increased from 20 to 80%. The sensitivity of vinyl chloride in this concentration range was affected greatly by the electrolyte composition.

Table 1 summarizes the performance of gold electrode at the appropriate potentials in various compositions of toluene/DMF solvent mixtures. The largest responding current, 100 μA, for 13% vinyl chloride gas was obtained at the applied potential of −2.3 V vs Ag/Ag$^+$ with the solvent of 50% toluene/50% DMF; the highest sensitivity, 3.42 μA %$^{-1}$, in the concentration range 13–34% was obtained at −2.3 V vs Ag/Ag$^+$ with the solvent of 20% toluene/80% DMF. However, the background

Fig. 6. Effects of solvent composition on the background current and responding current. Supporting electrolyte 0.01 M Bu$_4$NClO$_4$, hollow and solid symbols represent background and responding current, respectively. Testing gas 13% VCM gas. Toluene(%)/DMF(%): (○) 20/80; (●) 20/80; (△) 50/50; (▲) 50/50; (□) 80/20; (■) 80/20.
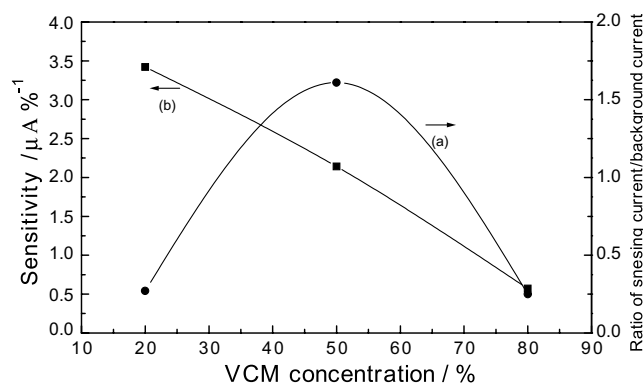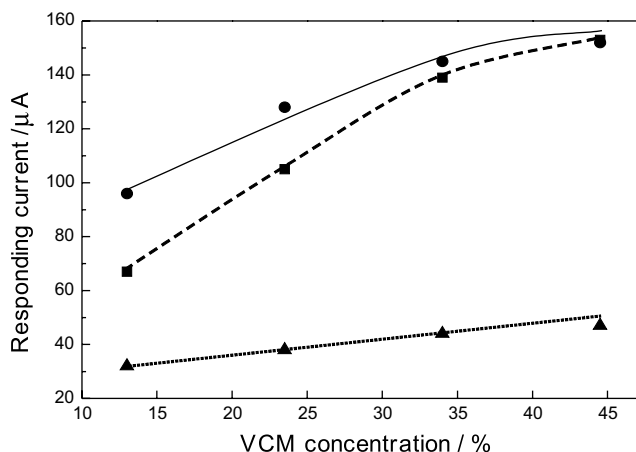

Fig. 7. Dependence of sensitivity and ratio of responding/background current on the solvent composition. Supporting electrolyte 0.01 M Bu$_4$NClO$_4$, applied potential −2.3 V vs Ag/Ag$^+$.

Table 1. Responding performance of Au/porous alumina plate/Pt assembly in various compositions of toluene/DMF solvent mixtures

Solvent composition Toluene%/DMF%	Appropriate potential for VCM reduction /V vs Ag/Ag$^+$	Responding current for 13% VCM* /μA	Sensitivity for 13–34% /μA %$^{-1}$
20/80	−2.3	67	3.42
20/80	−2.4	31	2.66
50/50	−2.3	100	2.14
50/50	−2.4	96	2.57
80/20	−2.3	32	0.57

*Obtained from polarization curve in Figure 7.

current obtained in the latter condition was the largest among these three solvent compositions.

4. Discussion

Water content in the electrolyte depends on the composition of the solvent mixtures because constituent solvents dissolve different amounts of water after storing for a long period. After analyzing with a moisture meter, the water contents in DMF and toluene were 6802 and 330 ppm, respectively. In the mixture of toluene and DMF, the water contents in the solutions containing 20%, 50% and 80% toluene were around 5641, 3353 and 2000 ppm, respectively.

If a small amount of water was dissolved in the toluene/DMF solvent mixture, the following three facts need to be considered:

(i) Water was electrolysed obviously at the working electrode while the applied potential was more negative than −1.8 V vs Ag/Ag$^+$ in the toluene/DMF mixture. The reduction process involved the uptake of two electrons per water molecule and formation of hydroxide ion and hydrogen. The background current in this study was suggested to be mainly due to cathodic current from water electrolysis. More water content in the electrolyte gave larger background current, and made the electrochemical reduction reaction of vinyl chloride less significant.

(ii) According to Fick's first law, the background current from water electrolysis is proportional to not only the concentration but also the diffusion coefficient of water in the electrolyte. The relation between diffusion coefficient of water (D) and viscosity of solution (η) can be expressed by Stokes–Einstein equation,

$$D = \frac{kT}{6\pi\eta a} \tag{1}$$

where k, T and a are the Boltzmann constant, absolute temperature and effective radius, respectively. The diffusion coefficient of water increases when the viscosity of the organic electrolyte decreases. As the toluene content in the mixture increases, the viscosity of mixture diminishes, based on the fact

that viscosity of toluene (0.56 cP) is lower than that of DMF (0.794 cP) [15]. Therefore, when the water concentration is the same, the cathodic current of water electrolysis increased with toluene content in the electrolyte due to the decrease of viscosity in the electrolyte mixture and the increase of diffusion coefficient of water.

(iii) The electrochemical reduction of each vinyl chloride molecule involved the uptake of one electron followed by the loss of a halide ion to yield a vinyl radical, which was then protonated and reduced [16]. The overall reaction is

$$C_2H_3Cl + H^+ + 2e^- \rightarrow C_2H_4 + Cl^- \tag{2}$$
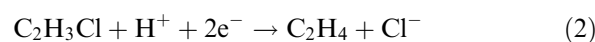
Water is one of the main proton donors in the organic electrolyte in this study. Therefore, the concentration of water in the organic electrolyte might be an important factor for the reduction of VCM.

Based on the above statements, water was required for VCM reduction, but it was also a source of background current. Table 2 lists the water contents and viscosities in the mixtures containing 20, 50 and 80% toluene, as well as the corresponding background currents at the applied potential of −2.3 V vs Ag/Ag$^+$. The largest background current, obtained from the electrolyte containing 20% toluene, may be explained by considering the fact that it contains the largest amount of water among the three solvent compositions. The background currents in 50% toluene/50% DMF mixture and 80%/20% mixture were about the same at the potential of −1.8 V vs Ag/Ag$^+$, and varied more significantly at more negative potentials, as shown in Figure 6. The background current of 50%/50% mixture was 62 μA, smaller than 123 μA in 80%/20% mixture. It was suggested that not only the water content but also the diffusion coefficient of water in the solvent mixture affected the background current. In the solvent mixtures containing 80% and 50% toluene, it was believed that the diffusion coefficient of water was more critical than the water content to the background current. The mixture with 80% toluene had smaller electrolyte viscosity and higher water diffusion coefficient, and hence had larger background current.

The responding currents in 20%/80% mixture (5641 ppm water) were smaller than those in 50%/50% mixture (3353 ppm water) when the potentials were more negative than −2.2 V, as shown in Figure 6.

Table 2. Water content and viscosity of various toluene/DMF mixture and obtained corresponding background current

Toluene content /%	H_2O content* /ppm	Viscosity[†] /cP	Background current[‡] /μA
20	5641	0.767	245
50	3353	0.725	62
80	2000	0.684	123

* Determined by moisture meter.
[†] Reference [6].
[‡] Obtained at applied potential −2.3 V vs Ag/Ag$^+$.

It suggested that water electrolysis increased greatly when the applied potentials were more negative than −2.1 V in 20%/80% mixture due to higher water concentration and thus diminished the reduction reaction of VCM. This also explained the fact that the ratio of responding current/background current in 20%/80% mixture was smaller than that in 50%/50% mixture, as shown in Figure 7, due to higher background current and lower responding current.

The new configuration, with one porous alumina plate and organic electrolyte, was shown to provide a feasible tool to determine the concentration of gaseous oxidative organic compounds, such as vinyl chloride, which could not be determined via the conventional metal/SPE electrode. The use of porous alumina plate not only provided three-phase reacting sites for reduction of vinyl chloride in gas phase but also diminished the faradaic reaction of electrolyte on the surface of working electrode. Furthermore, the background current would be diminished by proper choice of solvent or purification of solvent with vacuum distillation, molecular sieves [17], or neutral alumina powders [18]. Decreasing the background current would increase the ratio of the responding current to background current, and thus makes the configuration more promising for the development of sensors.

5. Conclusions

The new Au/porous alumina plate/Pt electrode assembly has been applied to the analysis of gaseous vinyl chloride with nonaqueous electrolyte. For acetonitrile medium as electrolyte, the sensitivity, response time, and recovery time on an Au electrode at −2.0 V vs Ag/Ag$^+$ were 0.63 μA %$^{-1}$, within 20 s, and 5 min, respectively. Compared with platinum, gold was a better electrode material for VCM reduction due to the smaller background current and larger response current. The sensitivities in the VCM concentration range 13–34% at the applied potential of −2.3 V vs Ag/Ag$^+$ increased with decrease in toluene content in the toluene/DMF mixture. The highest sensitivity, 3.42 μA %$^{-1}$, was obtained from the Au/porous alumina plate/Pt assembly with

20% toluene/80% DMF electrolyte. The ratio of response current/background current was found to vary as a function of electrolyte composition. The largest value of this ratio was 1.61, obtained from 50% toluene/50% DMF electrolyte mixture. The preferable electrode/electrolyte assembly, at the cost of a rather large ratio of response current/background current, will be suitable for development of a vinyl chloride detector.

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