

Conductivity Monitoring by an Amperometric Detector with a Cu(II)-Containing Poly(3-methylthiophene) Electrode

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Received May 12, 1989.

ABSTRACT

A conducting, chemically synthesized, Cu(II)-containing poly(3-methylthiophene) powder was pressed into a pellet and used as the working electrode of a three-electrode system in a thin-layer amperometric cell unit to detect ionic analytes in an aqueous stream by flow-injection analysis. The electrode response was linearly correlated with the applied voltage, which was varied between 0.2 and 3.0 V (vs. Ag/AgCl). It was shown that the electrode possesses favorable sensitivity and stability in comparison with other metallic electrodes such as stainless steel and Pt. During a period of more than a year, it showed no deterioration in its performance.

INTRODUCTION

It is known that chemical modification of electrode surfaces can alter the sensitivity of measurements by catalysis of the electrode reaction of the analyte as well as the selectivity through suppression of interfering electrode reactions [1]. In this respect, recent years have witnessed a growing interest in the utilization of various kinds of conducting polymers to modify the physico-chemical properties of electrodes used in flow-injection analysis (FIA) and liquid chromatography (LC).

Heineman and co-workers were first to employ an electrode coated with an electrochemically grown poly(pyrrole) film in a flowing liquid to detect otherwise electroinactive anions [2, 3]. In their measurements, the polymer electrode was kept under a positive potential during signal registration in an amperometric cell. Negative potential pulses were applied after each injection of analyte to undope the electrode. Similarly, Ye and Baldwin used a poly(aniline)-coated electrode at a relatively low applied potential. They employed a glycine buffer in order to minimize anion accumulation in the film [4].

The use of poly(benzylpropargylamine) as a potentiometric ion chromatography (IC) detector [5] and a poly(pyrrole) ion-selective electrode for chloride ions (6) are the latest examples of the use of conducting polymers. This type of modified electrode exhibits very promising electrochemical properties.

We have been working on both electrochemically grown [7-9] and chemically synthesized [10-14] poly(heterolene) materials in order to characterize their spectral and electrochemical properties. Among the several materials studied in our laboratory is the unusually stable Cu(II)-containing poly(3-methylthiophene), Cu(II)PMET. This material has been synthesized from 3-methyl-2,5-dilithiothienylene by using a CuCl₂ catalyst as reported elsewhere [15, 16].

This procedure resulted in a product where a certain amount of Cu(II) ions remain incorporated in an as yet unknown fashion in the polymer structure [10]. The chloroform insoluble fraction of Cu(II)PMET is remarkably stable; its conductivity increases about a millionfold when exposed to water and becomes as high as 40 S cm⁻¹ [10]. Swelling of its pressed disk in water was not observed [10], and leaching of Cu(II) ions into the aqueous solution was negligible (12).

The cyclic voltammogram of Cu(II)PMET in aqueous 0.1 M NaClO₄ supporting electrolyte shows two distinct peaks pertaining to the internal Cu(II)/Cu(I) redox couple, and no redox behavior of the thiophene ring itself is observed [12]. The amount of charge and its dependence on sweep rate also revealed that the copper,

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not only near the surface of the polymer but in the bulk, takes part in the redox reaction [12]. The shape of the peaks indicated a broad potential range of electrical conductivity in contrast to the polymer films produced on electrochemical oxidation of thiophene [17]. This polymer could be cycled for several weeks (approximately 10^5 times) without changing the shape of voltammogram or the magnitudes of the peak currents [12].

In this article we report on the analytical application of an electrode consisting of a pressed disk of Cu(II)PMeT in a cavity of a Kel-F block. The electrode was placed in an amperometric unit, and its responses toward various types of analytes were investigated under FIA conditions. The detector was shown to sense the ionic analytes on the basis of conductivity changes upon the passage of sample plugs. The Cu(II)PMeT electrode also exhibits significantly greater signal stability than either bare Pt or stainless steel (SS) electrodes used in the same detector unit.

EXPERIMENTAL

Reagents

Only reagent grade chemicals (Fisher Scientific Co.) and distilled and deionized water were used in the preparation of analyte stock solutions from sodium salts. The water and buffer solutions used as mobile phases were deaerated prior to their use in FIA. The polymer, Cu(II)PMeT, was prepared as described elsewhere [15].

Construction of the Polymer Working Electrode

A thin-layer cell for liquid chromatography from Bio-analytical Systems, Inc. (BAS) was modified to contain the Cu(II)PMeT electrode. The part of the BAS cell that contains the working electrode was replaced with a Kel-F block of identical shape and size. Two holes, each 3 mm in diameter with centers 4 mm apart, were drilled at the center of this block. Two stainless steel (type 316) plungers were manufactured to fit tightly into these holes; one of them was forced into one of the holes almost all the way through, and approximately 10 mg of Cu(II)PMeT powder was placed into the cavity formed at the tip of the SS plunger. The Kel-F block was then pressed against a flat stainless steel surface using a pressure of about 1000 psi to form a pellet of Cu(II)PMeT imbedded into the Kel-F block. The second SS plunger was pushed into the other hole until its tip was even with the surface of the Kel-F block. Both plungers were then sealed to the Kel-F block at the back end by means of a cyanoacrylate glue.

Flow Cell and Measurements

A PTFE gasket (0.38 mm thick) was placed between the previously described Kel-F block and a stainless steel cube (MF 1018, BAS) to form an electrochemical cell with a volume of about 10 μ L. The other relevant parts of the measuring system consisted of an Ag/AgCl (3 M NaCl) reference electrode (MF 2020) placed downstream in a

container (MF 1026), both manufactured by BAS. The stainless steel block that contained the carrier entrance and exit ports was functionalized as the auxiliary electrode. In a few experiments, however, the stainless steel pipe outlet mounted in the reference electrode container was used as the auxiliary electrode. The working electrode was either the Cu(II)PMeT electrode or the second SS plunger on the same block as explained previously. The block containing the working electrodes was placed in the cell in a parallel mode so that the flowing solution front would reach both electrodes simultaneously. In order to test the performance of a Pt electrode in the same configuration, a Teflon block holding a single Pt electrode (MF 2058, BAS) of the same diameter (i.e., 3 mm) was occasionally employed as the working electrode part of the cell.

The flow-injection system consisted of an Altex-100A double reciprocating pump followed with an Altex injection valve (Cat. No: 905-42). Teflon tubing (55 cm in length with a 0.3 mm i.d.) was used between the injection valve and the detector cell. A 20 μ L sample loop was used throughout the experiments. A BAS cyclic voltammetry unit (CV-1B) was employed to vary and control the potential applied to the working electrode. Peak-shaped current signals were recorded by an Omniscribe dual pen recorder from Houston Instruments.

For the measurement of the ac conductivities of solutions, a YSI (Yellow Spring Instruments Co., Inc.) Model 31A conductivity bridge with a YSI Model 3401 conductivity cell was used.

All of the potential values reported in this work are the set values indicated by the cyclic voltammetry unit and were applied vs. the Ag/AgCl (3 M NaCl) reference electrode.

RESULTS AND DISCUSSION

Nature of the Detector Response

It is generally believed that the signal on a positively held working electrode coated with a conducting polymer results from anion incorporation (doping) into the polymer film [2–4]. Contribution to the overall signal from conductivity changes in solution and in the polymer film, however, has been questioned. It was stated that finding an effective strategy to extract only the doping current from the response was a difficult task [3]. On the other hand, Ye and Baldwin [4] argued that observed responses on a poly(aniline) electrode could not be ascribed to conductivity increases associated with the passage of the analyte because the responses obtained under the same condition on a Pt electrode constituted only 3% of that of the polymer electrode.

Although not conclusive at this time, our results indicate that the signal generation in the previously described amperometric unit under FIA conditions, that is, employing highly resistive mobile phases (water, 0.3–0.6 μ S cm^{-1} ; 0.1 M glycine, 9.7 μ S cm^{-1} ; 5×10^{-4} M sodium *p*-hydroxybenzoate, 48.6 μ S cm^{-1}), is clearly more associated with conductivity changes that occur

TABLE 1 The Relationship between the ac Conductivities of Bulk Solutions and Their Detector Response in FIA^a

Sample (10 ⁻⁴ M)	Conductivity		Cu(II)PMeT Electrode				Pt Electrode	
	Measured ($\mu\text{s cm}^{-1}$)	Relative ^b	Auxiliary: SS Cube		Auxiliary: SS Pipe		Auxiliary: SS Cube	
			Signal (nA)	Relative ^b	Signal (nA)	Relative ^b	Signal (nA)	Relative ^b
NaF	8.8	0.81	3332	0.95	4.8	0.89	20	0.91
NaCl	10.8	1.00	3496	1.00	5.4	1.00	22	1.00
NaNO ₃	10.6	0.98	3468	0.99	5.2	0.96	18	0.82
Na ₂ SO ₄	23.0	2.13	4820	1.38	11.0	2.04	34	1.55
Na-ascorbate	6.6	0.61	2320	0.66	2.8	0.52	342 ^c	15.55
Na ₂ -oxalate	16.4	1.52	3623	1.04	7.8	1.44	32	1.45
Na ₃ -citrate	24.0	2.22	4732	1.35	12.6	2.33	66	3.00
Background			1000		4.6		16	

^a Mobile phase, water (1.0 mL/min); $E = 1.0$ V; volume injected, 20 μL . Signal values reflect the average of five measurements.

^b A value of 1.00 is ascribed to NaCl.

^c A faradaic current is implied for these sample types.

during analyte passage through the cell than with any other conceivable mechanism. It must be stressed here that *conductivity*, in the context of the previously described detector unit, is used in the sense that portrays the proportionality between applied potential and measured current. Although this term is not synonymous with the ionic conductances of the solutions measured with a conventional ac method, true conductance values need not be known in chromatographic analysis because the quantitation of analytes is done in reference to a calibration plot.

A series of experiments were designed to elucidate the signal generation. First, a set of data was obtained by measuring the bulk solution conductivities of various salts. These data were then compared with the detector current responses for the same analyte types when either the Cu(II)PMeT or the Pt electrodes were used as the working electrode (Table 1). A close correlation that was found between the two sets of data suggests to us that conductivity is the prevailing mode of response, especially when the Cu(II)PMeT working electrode is used in conjunction with the SS pipe as the auxiliary electrode. Comparatively, the set of data obtained using the Pt working electrode showed deviation for easily oxidizable analytes such as ascorbate. This observation implies that, with a detector other than the Cu(II)PMeT electrode, different electrochemical phenomenon as well as conductivity may be effective in signal generation.

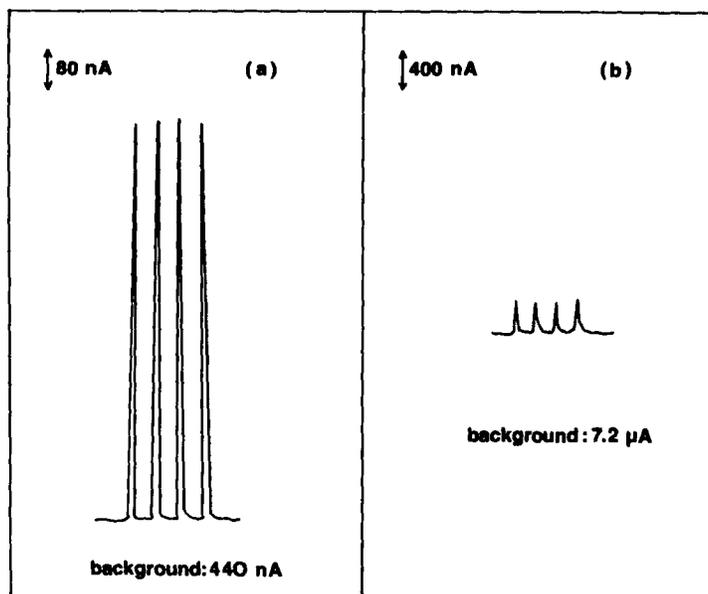
Second, in order to determine whether it was necessary for the analyte to have contact with the polymer working electrode for signal generation, a stainless steel pipe was installed between the injection valve and the thin-layer cell in an upstream position with respect to the working electrode. An air bubble was introduced into the water carrier through the sample loop, and the arrival times of this air bubble at the auxiliary pipe and the working electrodes were recorded. The translucent Teflon tubing employed in this experiment allowed the observation of the air bubble through the system. It was observed that signal generation was achieved when the

analyte plug was about at the midpoint between the auxiliary and the working electrodes. Obviously, the signal was shown to form before the analyte had reached the working electrode, so the question of analyte doping into the polymer film could clearly be dismissed.

When water was injected into mobile phases having greater conductivity than water, a negative peak corresponding to a decrease in background was observed. The same phenomena was observed on both the Pt and the polymer electrodes while the 5×10^{-4} M sodium *p*-hydroxybenzoate or 0.1 M glycine were used as the carrier. In fact, the 5×10^{-4} M sodium *p*-hydroxybenzoate used in this experiment represents a typical mobile phase concentration employed for single-column ion chromatographic (SCIC) separations. In order to test the viability of the Cu(II)PMeT electrode while employing this moderately conducting mobile phase, 20 μL 10^{-4} M NaCl and NaNO₃ solutions were introduced into the system. The same mobile phase composition was used to prepare the analyte solutions in order to eliminate the so called water dip, which would interfere with signals to be measured. Examples of FIA runs for NaNO₃ with both the water and sodium *p*-hydroxybenzoate carriers are given in Figure 1. With the latter carrier, a large increase in background current with accompanying decrease in signal height is observed. This is, of course, typical with conductivity detectors used in ion chromatography.

Our results, which indicate that an amperometric detector may under certain conditions behave as a dc conductance monitor, does not constitute the first example of this type. It has been reported that an amperometric detector with an Ag electrode placed after the suppressor column in an ion chromatographic system responds not only to electrochemically active analytes but also to inactive ions such as F⁻, NO₃⁻, PO₄³⁻, and SO₄²⁻, and the detection limits are reported to be better than those obtained by conductimetry [17–19]. Observed responses were ascribed to the pH changes of eluents as they pass through the suppressor where cations were exchanged for hydronium ions [19].

FIGURE 1. Examples of FIA signals obtained on the Cu(II)PMeT electrode, mobile phase. (a) Water: background current, 440 nA; (b) 5×10^{-4} M sodium *p*-hydroxybenzoate (pH = 8.5): background current, 7.2 μ A.



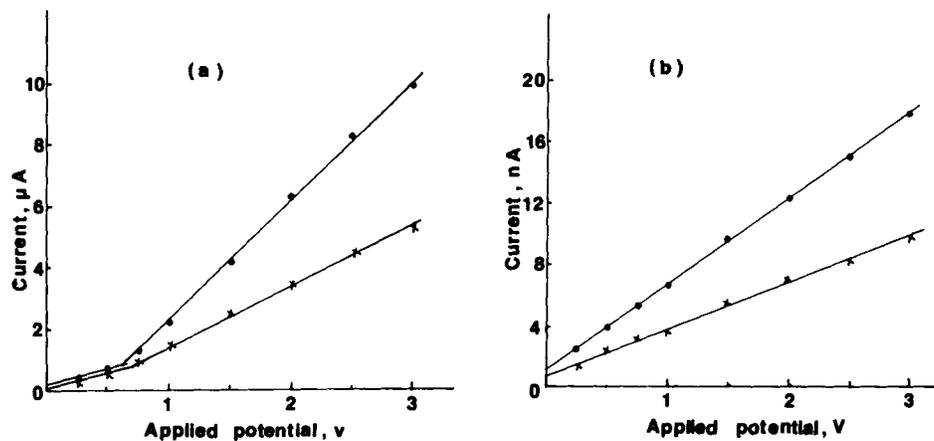
In thin-layer electrochemical cells, ohmic polarization of the electrodes is an important consideration in cell design, and uncompensated IR drop and the total cell resistance should be minimized by suitably adjusting the resistance of the flowing solution. The design and other electrochemical criteria could conveniently be satisfied with large cells commonly used for measurements in quiescent solutions. With FIA and LC detectors, however, these criteria are usually neglected because the effective volume of the cell and the hydrodynamics are more important from the point of view of the analyte zone dispersion [20].

In the cell configuration that we use, the working and the large auxiliary (stainless steel cube) electrodes were placed facing each other with a minimal space between them so as to minimize the IR drop of the cell. It is highly likely, however that, with the low conducting mobile phases employed, the cell could still be experi-

encing large IR drops. When the analytes are introduced, total cell resistance drastically changes and results in a current signal. As a matter of fact, a large decrease in background currents with a concomitant diminution of peak heights was observed when the pipe mounted on the container was used as the auxiliary electrode. Although the cell volume was now much higher, the observed decreases in peak heights cannot be explained by the zone dispersion alone. Elevation of the total cell resistance through a larger distance between electrodes is a more reasonable answer. The effect of electrode spacing on the signal height and background relation with the two types of auxiliary electrodes are depicted in Figure 2.

It must be pointed out that the dc conductance behavior of this detector is not exclusive to the Cu(II)PMeT electrode; similar behavior is also observed with Pt or SS electrodes when the analytes are not

FIGURE 2. The effect of electrode spacing as a function of applied potential on the background (\times) and signal (\bullet) currents for the Cu(II)PMeT electrode. Stainless steel cube (a) and pipe (b) were used as auxiliary electrodes. Sample: 20μ L 10^{-4} M NaNO₃; mobile phase: water, 0.5 mL/min.



oxidizable at the potentials applied. Analytical parameters describing the electrode performances, however, vary a great deal with the type of the electrodes employed.

Performance Comparison of Cu(II)PMeT, Stainless Steel, and Pt Electrodes

In order to test the effect of varying applied potential on the signal magnitude, $20 \mu\text{L } 10^{-4} \text{ M NaCl}$ and NaNO_3 solutions were injected into water carrier flowing at a flow rate of 0.5 mL/min . A plot of signal height versus applied potential produced a curve with two linear regions having slightly different slopes when Cu(II)PMeT was the working electrode (Figure 2a). The upper linear portion of the curve, which appeared above approximately 1.5 V , was steeper. Similar phenomena were observed with both SS and Pt electrodes; in both cases, however, the upper portion of the curves were much steeper in comparison with the Cu(II)PMeT electrode. Background and signal values obtained with SS and Pt electrodes as a function of applied potential are given in Figure 3. It is interesting to note that background readings followed the same trend as the respective analyte signals on corresponding electrodes. The sudden rise in background currents observed at a potential slightly above 1.7 V can be ascribed to oxidative breakdown of water on Pt and SS electrodes. It is probable that, with these electrodes and at certain higher potentials, the current signals are an additive function comprising conductivity changes and, perhaps to a greater degree, a true faradaic signal resulting from water decomposition. The almost linear rise in the background current observed with the Cu(II)PMeT electrode, on the other hand, suggests once again that the prevailing mode of the response of the detector with this electrode is conduc-

tivity [21]; thus, faradaic contribution to the observed signals can be considered as negligible.

Passivation of electrodes in electrochemical detectors used in LC has deleterious long-term effects upon the measurements. Recently reported results [22] indicate a gradual increase in response to a dc conductivity detector with SS electrodes, which possibly are due to an increase in the electrode area from anodic corrosion. We witnessed a similar observation with the SS electrode used in our work. The reproducibility of SS and polymer electrodes were tested by repeatedly injecting a $20 \mu\text{L } 10^{-4} \text{ M NaCl}$ solution. A total of 100 injections over a period of 6 hours were made in each case (a potential of 0.5 V was applied to both). The average of the first 10 injections was $386 \pm 10.6 \text{ nA}$, and the same value for the last 10 was $620 \pm 8.6 \text{ nA}$ on the SS electrode, which represents a 1.6-fold increase in current. Corresponding figures for the Cu(II)PMeT electrode were 184 ± 1.2 and $186 \pm 2.0 \text{ nA}$, respectively, indicating a significant improvement in detector response stability.

A typical Cu(II)PMeT electrode unit has been in use for more than 12 months with no apparent deterioration of its performance even under moderately high potentials and with many diverse types and concentrations of ionic analytes. When subjected to potentials above 1.0 V , the stainless steel electrode, on the other hand, exhibited severe discoloration on its surface, especially when NaCl was used as the analyte. With the mobile phases of higher ionic nature than the usually employed water, the degree of discoloration was more severe.

It must be emphasized at this point that performances of the three electrodes [Pt, SS, and Cu(II)PMeT] are studied only to distinguish their response behavior and stability in the amperometric unit employed. At this stage, we did not attempt to compare the performance of Cu(II)PMeT electrode with that of the true ac conductivity detectors employing SS or Pt electrodes.

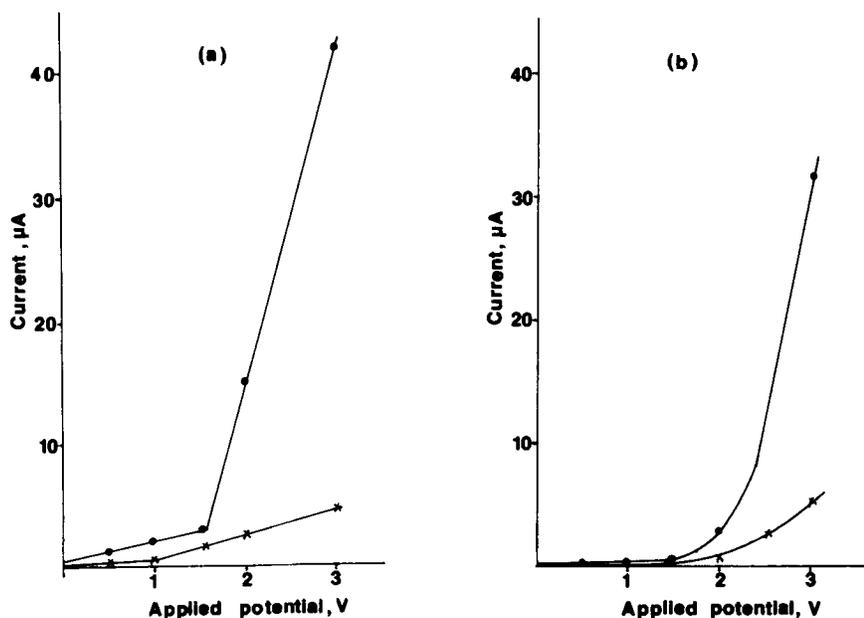
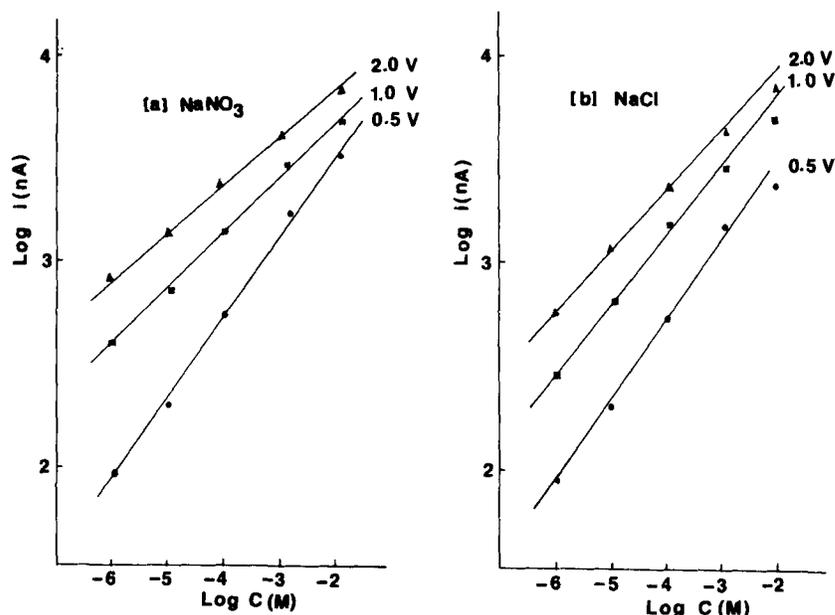


FIGURE 3. The effect of applied potential on the background (x) and signal (●) currents for stainless steel (a) and platinum (b) working electrodes. AE is the SS cube in both cases. Sample: $20 \mu\text{L } 10^{-4} \text{ M NaNO}_3$; mobile phase: water, 0.5 mL/min .

FIGURE 4. Calibration curves obtained with the Cu(II)PMeT electrode for $20 \mu\text{L } 10^{-4} \text{ M NaNO}_3$ (a) and $20 \mu\text{L } 10^{-4} \text{ M NaCl}$ (b) at three different potentials. Mobile phase: water, $0.5 \mu\text{L}/\text{min}$.



Sensitivity and Linearity of the Polymer Electrode

The linearity of the Cu(II)PMeT electrode was indeed very good for the NaCl, NaF, NaNO₃, and NaI analytes, and a log–log relationship was shown to exist between the signal height and the amount of material injected. The typical calibration curves for NaCl and NaNO₃ obtained at three different applied potential values that are shown in Figure 4 indicate a linear range of over three orders of magnitude for the analyte types considered.

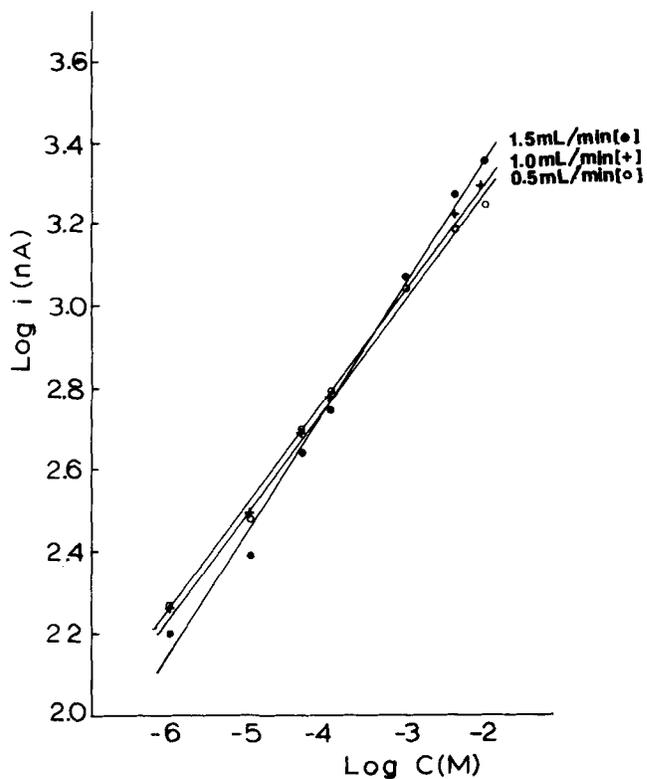
Detection limits in conductivity detection are determined by the background conductivity of the mobile phases because it determines the sensitivity of the detection system. For that reason, the detection limit of our unit employing the Cu(II)PMeT polymer electrode was evaluated for one of the aforementioned analyte types, namely NaNO₃, using two different mobile phases with vastly different background conductivities. Distilled, deionized, deaerated water and $5 \times 10^{-4} \text{ M } p$ -hydroxybenzoate solution with background values of 460 and 4500 nA, respectively, were chosen as the mobile phases. Applied potential was 1.0 V, and the flow rate of the carrier was 0.5 mL/min. When the water was used as the mobile phase, the detection limit (3 s) for NaNO₃ was calculated as $2.0 \times 10^{-8} \text{ M}$; on the other hand, a value of $6.2 \times 10^{-6} \text{ M}$ was obtained when the latter mobile phase was employed.

Although the signal magnitudes observed with the SS electrode, even under 1.5 V applied potentials, were relatively higher than those obtained on the polymer electrode, the latter yielded a much better signal-to-noise ratio. On the entire potential region studied, the bare Pt electrode produced responses that, depending on the electrode potential, comprised approximately 1–10% of those of the polymer electrode, and, as was the case with the SS electrode, the polymer electrode furnished supe-

rior signal-to-noise ratio values when compared with the Pt electrode.

The flow rate dependency of the signal was also tested with the Cu(II)PMeT electrode. Signal heights obtained with injections of a $20 \mu\text{L } 10^{-4} \text{ M NaNO}_3$ solution

FIGURE 5. Log (signal) versus log (concentration) relationship at three different flow rates of water carrier. $E = 0.5 \text{ V}$; sample, $20 \mu\text{L NaNO}_3$.



displayed virtually no dependence on the mobile phase flow rate (Figure 5), which is consistent with a pure conductance response.

In conclusion, we report that this method of operating the already existing amperometric detectors provides a low-cost, and simple means of monitoring the solution conductivity based on dc current. It is possible that it may conveniently be applied in FIA and suppressed-ion chromatography as well as in single-column IC with eluents of low ionic strength. We also think that the sensitivity and stability of the metallic electrodes of amperometric detectors used in the previously described way can be increased substantially by the utilization of metal incorporated conducting polymers as described in this work.

ACKNOWLEDGMENTS

This work was supported by the Edison Sensor Technology Center.

REFERENCES

1. R. W. Murray, in *Electroanalytical Chemistry*, Vol. 1, A. J. Bard, ed., Marcel-Dekker, New York, 1983, pp. 191–367.
2. Y. Ikariyama and W. R. Heineman, *Anal. Chem.* **58** (1986) 1803.
3. Y. Ikariyama, C. Galiatsatos, W. R. Heineman, and S. Yamachi, *Sens. Actuators*, **12** (1987) 455.
4. J. Ye and R. P. Baldwin, *Anal. Chem.* **60** (1988) 1979.
5. L. Campenalla, T. Ferri, M. Majone, T. Mihic, M. V. Russo, and A. M. Salvi, in *Recent Developments in Ion Exchange*, P. A. Williams and M. J. Hudson, eds., Elsevier, London, 1987, pp. 315–21.
6. S. Dong, Z. Sun, and Z. Lu, *Analyst*, **113** (1988) 1525.
7. L. Laguren-Davidson, C. V. Pham, H. Zimmer, and H. B. Mark, Jr., *J. Electrochem. Soc.* **135** (1988) 1406.
8. D. D. Cunningham, A. Galal, C. V. Pham, E. T. Lewis, A. Burkhardt, L. Laguren-Davidson, A. Nkansah, O. Y. Ataman, H. Zimmer, and H. B. Mark, Jr., *J. Electrochem. Soc.* **135** (1988) 2750.
9. A. Czerwinski, H. Zimmer, C. V. Pham, and H. B. Mark, Jr., *J. Electrochem. Soc.* **132** (1985) 2669.
10. A. Czerwinski, H. Zimmer, A. Amer, C. V. Pham, S. Pons, and H. B. Mark, Jr., *J. Chem. Soc., Chem. Commun.* (1985) 1158.
11. A. Czerwinski, H. Zimmer, C. V. Pham, A. Amer, J. R. Schrader, and H. B. Mark, Jr., *Anal. Lett.* **18** (1985) 673.
12. A. Czerwinski, D. D. Cunningham, A. Amer, J. R. Schrader, C. V. Pham, H. Zimmer, and H. B. Mark, Jr., *J. Electrochem. Soc.* **134** (1987) 1158.
13. A. Czerwinski, L. Laguren-Davidson, C. V. Pham, H. Zimmer, and H. B. Mark, Jr., *Anal. Lett.* **18** (1985) 2395.
14. A. Czerwinski, C. V. Pham, D. D. Cunningham, L. Laguren-Davidson, H. Zimmer, and H. B. Mark, Jr., *J. Electrochem. Soc.* **133** (1986) 576.
15. A. Amer, H. Zimmer, K. J. Mulligan, H. B. Mark, Jr., S. Pons, and J. F. McAleer, *J. Polym. Sci., Polym. Lett. Ed.* **22** (1984) 77.
16. C. V. Pham, A. Czerwinski, H. Zimmer, and H. B. Mark, Jr., *J. Polym. Sci., Polym. Lett. Ed.* **24** (1986) 103.
17. G. Tourillon and F. Garnier, *J. Electrochem. Soc.* **130** (1983) 2042.
18. G. T. Tarter, *Anal. Chem.* **56** (1984) 1264.
19. G. T. Tarter, *J. Liq. Chromatog.* **7** (1984) 1559.
20. K. Stulik and V. Pacakova, *Electroanalytical Measurements in Flowing Liquids*, Ellis Horwood, New York, 1987.
21. D. Kaurilova, K. Slais, and M. Krejci, *Coll. Czech. Chem. Commun.* **48** (1983) 1129.
22. D. Qi, T. Okado, and P. K. Dasgupta, *Anal. Chem.* **61** (1989) 1387.