The spectra of the copolymer film and the PVC–PVAc film of the same composition were almost identical with respect to band position. The spectrum of the copolymer in KBr was the same as that of the copolymer film, but the peaks were broader (Figure 1). From previous assignments of the spectra of PVC (3) and PVAc (1), the band at 5.74 microns (1744 cm.$^{-1}$) was inferred to be the C=O stretching vibration, and that at 7.02 microns (1425 cm.$^{-1}$) to be the CH_2 scissors vibration.

Calibration curves prepared from the five types of intensity data are shown in Figure 2. The curves obtained with Types B and C for films were linear and passed through the origin. Other types of intensity data gave curved lines. No linear relations were found for samples prepared as KBr pellets. The qualitative degree of linearity of each curve is shown in Table I. For PVAc concentrations greater than 3%, the nonlinear relations shown in Figure 2 can be made linear by using the logarithm of the intensity ratio. It is concluded that the PVAc content of the copolymer is proportional to the ratio or to the logarithm of the ratio. Calibration curves of PVC and PVAc mixtures gave the same results as those of the copolymer film samples, and it is possible to use the calibration curve of the mixtures for the determination of the copolymer composition.

The regression lines of the calibration curves were tested using the method of Youden (5). All standard deviations were within 0.5%. To check the replicability of any point on the lines, five films and pellets of the same sample were prepared and the spectra were measured under identical conditions. The relative error of absorbance ratios of the two bands was within 0.6% (0.3% for films, 0.6% for pellets). The thickness of the films and the sample concentration in the pellets had no effect on the precision of the measurements.

In summary, Types B and C intensity data are the preferred ones. Samples can be prepared quickly and easily by the KBr pressed disk technique, but the results from the films are more accurate.

LITERATURE CITED

(1) Elliott, A., Ambrose, E. J., Temple, R. B., J. Chem. Phys. 16, 877 (1948).
(2) Grisenthwaite, R. J., Plastics 27, 117 (1962).
(3) Narita, S., Ichinohe, S., Enomoto, S., J. Polymer Sci. 22, 95 (1956).
(4) Wiberley, S. E., Sprague, J. W., Campbell, J. E., ANAL. CHEM. 29, 210 (1957).
(5) Youden, W. J., Ibid., 19, 946 (1947).

Tsugio Takeuchi
Sadao Mori

Institute of Techno-Analytical Chemistry
Faculty of Engineering
Nagoya University
Nagoya, Japan

Operational Amplifier System for Cyclic Chronopotentiometry

Sir: Cyclic chronopotentiometry (CC) is a useful tool for measurement of the rate constants of chemical reactions associated with electrode processes (2–5). This technique allows the mechanism of chemical reactions to be inferred from the trend in transition time ratios; rate constants can be calculated from these ratios and the value for the first transition time. The previously reported instrumentation (3) used plate circuit relays to switch the current at the appropriate potentials. However, when the measured transition time is of the order of 10 times the relay switching time, relays cannot be used. Since many rate constants are sufficiently fast to preclude the use of the above mentioned circuit—e.g., the rate constant for the reaction of titanium(III) with chlorate ion (9) would require transition time measurements of about 1 msecond—a circuit for CC based on operational amplifiers was devised.

Operational amplifiers have been used successfully in recent years to perform many electrochemical measurements. Their fast response and reliability make them ideal for this purpose. The present communication describes a circuit for CC using operational amplifiers, which allows current reversals in much less than 1 msecond.

EXPERIMENTAL

The circuit diagram is shown in Figure 1. The operational amplifiers were either four Philbrick K-2W amplifiers in a Philbrick 6009 manifold or a Heath EUW-19A operational amplifier system. Both arrangements worked well. The wiring and values of the component parts, wire wound potentiometers and composition resistors, were not critical. When K-2W amplifiers are used, up to 1.8 ma. can be supplied to the cell. This figure can be increased to 20 ma. by using SK2-B booster followers on amplifiers 2 and 3.

The chronopotentiometric cell followed current practice. A hanging mercury drop electrode was used as the working electrode so that high current densities could be produced without using booster amplifiers. In most cases it was not necessary to know the area of the electrode in order to measure chemical kinetic parameters. Most of the measurements were made at times less than 5 seconds so that nonlinear diffusion was unimportant. Both the auxiliary and reference electrodes were calomel electrodes. The experiment was begun by unshorting the working and auxiliary electrode with a mercury-wetted relay, and the potential–time curves were followed with an oscilloscope (1). The transition times were determined with the oscilloscope or with a digital counter in the time interval mode (5).
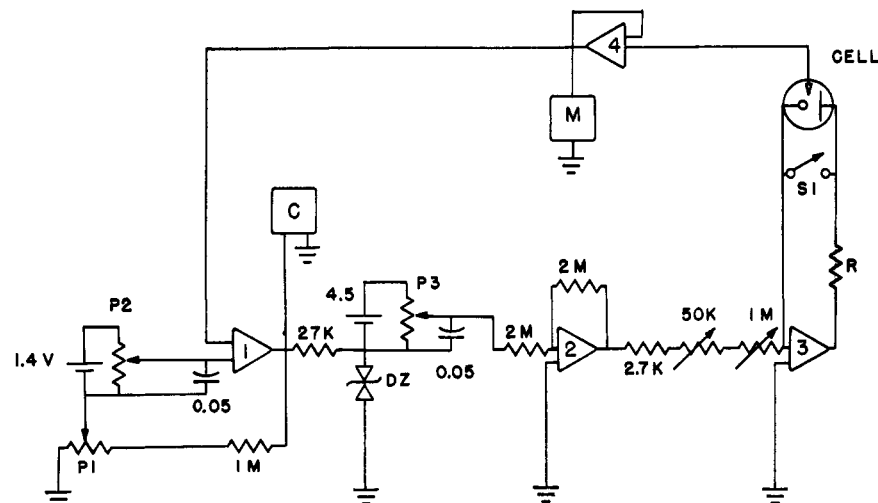

Figure 1. Circuit for cyclic chronopotentiometry

P1, 15K; P2, P3, 1M; DZ, 6.3-volt double anode Zener diode, Radio Shack 2761037; S1, mercury-wetted relay, Potter-Brumfield JM 2-11122; C, digital counter trigger input; M, oscilloscope; R, current measuring resistor, 1000 ohms, 0.05%

RESULTS AND DISCUSSION

The circuit consists of two main parts: a constant current source and a potential switch. The constant current source, based on operational amplifier 3, is conventional (6, 8). The current through the cell is given by the voltage appearing at the output of amplifier 2 divided by the total resistance at the input of amplifier 3. The current through the cell remains constant, up to the voltage limits of the operational amplifier, regardless of the resistance and voltage changes in the cell during the electrolysis.

Amplifier 1 is wired as a potential switch or detector with hysteresis (7). The output of amplifier 1 is either $+50$ volts or -50 volts depending upon the voltage at the input terminals. A portion of the output voltage, e_c, is fed back to the input through $P1$, and a reference voltage, e_{ref}, is also added to this input terminal (the reference input) with $P2$. Switching occurs when the voltage on the other input terminal, e, is $e_{ref} + e_c$ (the sign of e_c changes as the sign of output voltage changes). For example, if e_{ref} is $+1.0$ volt, and e_c is 0.5 volt, switching occurs at 0.5 and 1.5 volts. When e is positive with respect to the reference input terminal, the output voltage is -50 volts, e_c is -0.5 volt, and the potential on the reference input terminal is 0.5 volt. Switching occurs when e drops just below 0.5 volt. Now the output voltage is $+50$ volts, e_c is $+0.5$ volt, and the potential on the reference input terminal is 1.5 volts. Switching will next occur when e is 1.5 volts. This type of switch has also been used recently in a triangular sweep generator (10).

The output voltage of amplifier 1 is changed to a strictly constant ± 6.3 volts by the double Zener diode. This voltage is inverted and forms the input voltage to the constant current source. $P3$ allows the ratio of anodic to cathodic current to be varied. The input voltage, e, is the potential of the reference electrode with respect to the working electrode, connected through a follower amplifier.

For a system with no kinetic complications—e.g. cadmium ion in potassium nitrate—the first transition time was 62 msecond and the subsequent times were even less. This measurement could not have been made using the previously described circuit (3), since the switching time would have been an appreciable part of the measured transition times. The calculated times were in the predicted ratios (3), 1.00, 0.33, 0.59, etc. This circuit has been used successfully to study the current reversal and cyclic chronopotentiometry of systems following the E.C.E. mechanism, such as p-nitrosophenol, p-nitrophenol and o-nitrophenol and to study the reduction of titanium(IV) in the presence of hydroxylamine; details of these studies will be presented elsewhere.

LITERATURE CITED

(1) Bard, A. J., ANAL. CHEM. **33**, 11 (1961).
(2) Bard, A. J., Herman, H. B., Third International Congress of Polarography, The Polarographic Society, Southhampton, England, July 1964.
(3) Herman, H. B., Bard, A. J., ANAL. CHEM. **35**, 1121 (1963).
(4) Herman, H. B., Bard, A. J., *Ibid.*, **36**, 971 (1964).
(5) *Ibid.*, p. 510.
(6) Malmstadt, H. V., Enke, C. G., "Electronics for Scientists," p. 369, Benjamin, New York, 1963.
(7) G. A. Philbrick Researches, Inc., Boston, Mass., "Applications Manual for Philbrick Octal Plug—In Computing Amplifiers," p. 19, 1957.
(8) Reilley, C. N., *J. Chem. Educ.* **39**, A853 (1962).
(9) Smith, D. E., ANAL. CHEM. **35**, 610 (1963).
(10) Weir, W. D., Enke, C. G., *Rev. Sci. Instr.* **35**, 833 (1964).

HARVEY B. HERMAN[1]
ALLEN J. BARD
Department of Chemistry
The University of Texas
Austin, Texas 78712

[1] Present address, Department of Chemistry, University of Georgia, Athens, Ga. 30601.

Polarographic Determination of o-Phenylenediamine

Increase in Sensitivity by Employing Lithium Iodide as Supporting Electrolyte

SIR: Recently there has been considerable interest in the development of analytical methods for the determination of small amounts of o-phenylenediamine (1, 3, 6, 7, 11). Interest in this compound arises from its widespread applications as a synthetic intermediate and anti-oxidant (1, 4). An electrometric method, based on the catalytic polarographic prewave [thought to involve the reduction of a Ni complex which is regenerated in a cyclic manner (8, 10)] observed when Ni(II) is reduced at a dropping mercury electrode in the presence of small quantities of o-phenylenediamine, has been reported (7). The maximum sensitivity with acceptable precision was about $1 \times 10^{-5}M$ o-phenylenediamine. This paper reports the effects of both the nature and concentration of supporting electrolyte on the sensitivity of this indirect polarographic method. The sensitivity can be increased to allow o-phenylenediamine to be determined in the $10^{-7}M$ range with acceptable precision by using LiI in $0.1M$ concentration as the supporting electrolyte.

EXPERIMENTAL

Apparatus. The dropping mercury electrode (D.M.E.) used in the analytical determination experiments had a drop time of 4.13 seconds at a height of 118.2 cm. of mercury in $0.1M$ LiI with no applied potential. Under these conditions the outflow of mercury was 0.816 mg. per second. The polarograms of Figure 1 were recorded using a D.M.E. with a drop time of 9.38 seconds in air free distilled water at a height of 66.2 cm. with no applied potential; the outflow of mercury was 0.456 mg./sec. The actual drop time of the D.M.E. during the measurement was mechanically controlled at 4.00 ± 0.05 seconds by means of an electronically controlled hammer (2). A saturated calomel electrode (S.C.E.) was used as the reference electrode, and its electrical contact with the sample solution in the polarograph cell was made through an agar-agar KCl bridge.

The polarograms were obtained with a Leeds & Northrup Type E Electrochemograph with no damping. All other experimental conditions and the preparation of reagents were the same as described previously (7), except Ca^{+2} ion was not added as a maximum suppressor (7, 10); see below. The pH of the solutions was monitored by a Leeds & Northrup pH meter using miniature glass and calomel electrodes in the polarograph cell, throughout the polarographic measurement.

RESULTS AND DISCUSSION

Figure 1 shows the polarograms obtained for solutions of $5 \times 10^{-4}M$ Ni(ClO$_4$)$_2$. Curves A and C contain $1.0M$ NaAc buffer (pH = 5.5) and $6 \times 10^{-3}M$ Ca(Ac)$_2$ [same solution conditions employed in previously reported polarographic method for o-phenylenediamine (7)] and curves B and D contain $0.1M$ LiI (pH = 7.1). Curves C and D con-