

Effects of Maxima Suppressors on Polarographic Diffusion Currents

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The influence of maxima suppressors on the polarographic diffusion current has been reinvestigated. Abnormally large values for the diffusion current are found in the absence of suppressor. The amount required to suppress maxima is less for large electrodes at longer drop-times. The depressive action of large excesses of suppressor also has been studied. Agar is shown to be an effective suppressor of maxima and a sufficient amount can dissolve in a short period of time, when using H-cells containing agar plugs, to completely suppress maxima. As a result, quantitative studies of suppressor action with this type of cell are of doubtful significance.

1. Introduction

Polarographic measurements have gained widespread acceptance in analytical chemistry because of the direct proportionality between the diffusion current and the concentration of material responsible for the electrode reaction. Most applications have made use of comparative methods or empirical relationships in which only a reproducible value of the current is required. The theoretical expression for the current and the conditions under which it is applicable are of interest to the analytical chemist because of the minimization of calibration experiments that would result from its use. Moreover, for evaluation of diffusion coefficients, half-wave potentials, and related quantities, it is necessary that theoretically exact and experimentally defined conditions be employed.

An earlier publication [1]¹ discussed the conditions for application of the Ilkovic equation to polarography. It was shown that the presence of maxima on polarographic waves severely complicated their theoretical interpretation but that addition of suppressors greatly improved the situation. These observations are in qualitative agreement with much work found in the literature, and it is common practice to include a suppressor in polarographic supporting electrolytes. Recently Meites and coworkers [2] reported that more satisfactory results are obtained when suppressors are not in the solution. The purpose of the present paper is to reexamine the relation of the polarographic diffusion current to experimental conditions under which it is obtained.

2. Experimental Details

A Sargent-Heyrovsky polarograph model XII was used for part of the measurements, whereas the remainder were made with a manual arrangement similar to that described by Müller and Petras [3]. For the latter, the source of electromotive force across the polarographic cell was a high-precision potentiometer. The Aryton shunt and the galvanometer of a Heyrovsky-Nejedly polarograph, model VIII, were used together with a lamp and scale for measurement of the current. The galvanometer was

calibrated immediately after each polarographic measurement, by passing through it a current of approximately the same magnitude, standardized by potentiometric measurement of its current-resistance drop across a standard resistance.

For the calibration of the polarograph, the method of Ladisch and Balmer [4] was used. This consisted in passing a known current into the galvanometer and recording the deflection produced on the photographic paper. This current was chosen to produce marks in close proximity and of similar magnitude to the wave so that, after development of the record, a direct comparison could be made. In this manner, errors due to dimensional changes in the paper and nonlinearity of galvanometer deflections were minimized.

The circuit shown in figure 1 was used to make the calibrations described above. The terminals marked *POL* were connected directly to the shunt of the galvanometer by suitable connections, and a precision potentiometer was connected to *POT*. Standard resistance *R* was a five-dial, 10,000-ohm resistance box. The radio-type potentiometers *P*₁, *P*₂, *P*₃, and *P*₄, were equipped with 100-division dials. Potentiometer *P*₁ was set at a reading of 100, and the others were adjusted until a deflection of approximately 100 mm was obtained for the galvanometer. The dial of *P*₁ then read directly in millimeters and could be used conveniently to obtain any deflection desired. By noting the galvanometer deflections just preceding and following the wave, it was easy to duplicate them with a known current for calibration purposes. The circuit was used with the

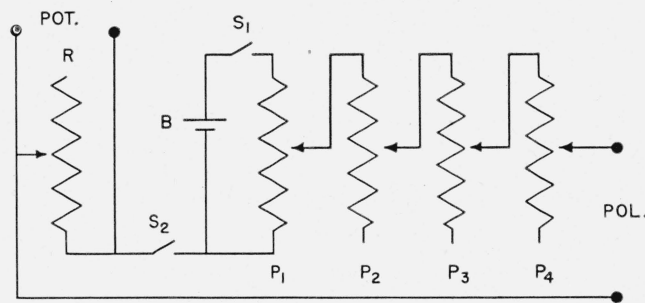


FIGURE 1. Circuit used for calibration of polarographic equipment.

¹Figures in brackets indicate the literature references at the end of this paper.

switch of the polarograph in the "open" position. The galvanometer was then independent of the polarograph, and straight lines of any desired length could be recorded corresponding to a given deflection of the galvanometer.

Dropping-mercury electrodes of three different sizes were used. Marine barometer tubes gave drops of about 7 mg in mass and drop times in the range 0.7 to 7 sec. Electrodes with drops of masses 26 and 70 mg, respectively, and drop times up to 7 sec were prepared, as shown in figure 2. Capillary tubing of 0.2-mm bore was softened and thickened in a flame to give the required resistance to flow. By placing the constriction, *C*, in the upstream direction no difficulty in interruption of flow was experienced. The tips were drawn down to obtain the desired size of drop. After a few trials, electrodes having the required characteristics were readily fabricated. They were sealed to a standpipe equipped with a side arm for attachment of a mercury-leveling bulb.

The anodes were silver wires wrapped around the dropping-mercury electrodes [5]. This type of anode is preferred wherever it is applicable because it does not introduce foreign impurities in the solution.

Nitrogen purified by passage over heated copper was used for the removal of oxygen from the solutions. Tall-form, lipless beakers of 100-ml capacity served as cells. These were fitted with rubber stoppers containing tubes for the introduction of nitrogen through or over the solution and with an inverted funnel as used by Lingane and Kolthoff [6] for the collection of drops from the electrode. By this arrangement, measurements of the *m* value were made for each measurement. Drop times were clocked with a stop watch at the potentials where diffusion currents were measured. All cells were immersed in a water bath thermostatted at $25.00^\circ \pm 0.02^\circ\text{C}$.

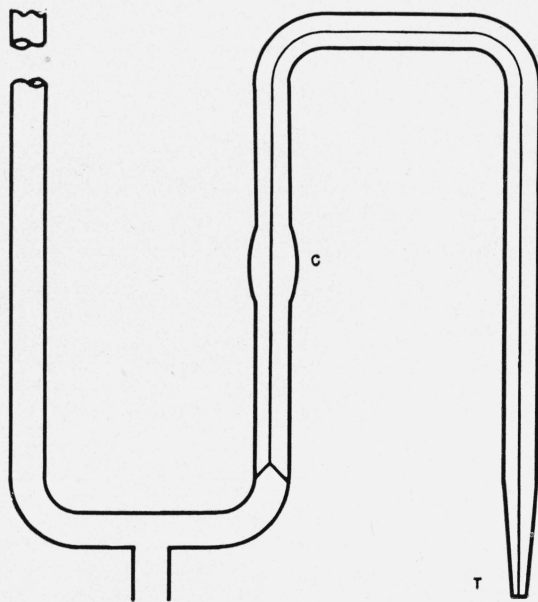


FIGURE 2. Design for dropping-mercury electrode.

Measurements of the wave heights were made by the exact method in the manner and with the device described previously [7]. Measurements of the residual current were made for each supporting electrolyte used and for each electrode and drop-time employed.

All the cells and glassware were scrupulously cleaned and bathed in live steam for a period of about 10 min. to remove traces of cleaning agents and suppressors from previous experiments.

3. Results

Direct intercomparisons of values for the diffusion current cannot be made because of their variation with the concentration of the solution and with the size of drop and rate of dropping of the electrode. To correlate the results found in this work, the Ilkovic equation was used and values for the diffusion-current constant, $I = i_d/Cm^{2/3}t^{1/6}$, were calculated from the measurements. Recently, Strehlow and Stackelberg [8] and Lingane and Loveridge [9] have shown that a somewhat more complicated equation expresses the experimental data more precisely. However, the conclusions of this paper are not affected by any small defect of the Ilkovic equation in the expression of the diffusion current.

Values of the diffusion-current constant calculated from measurements of cadmium solutions in a

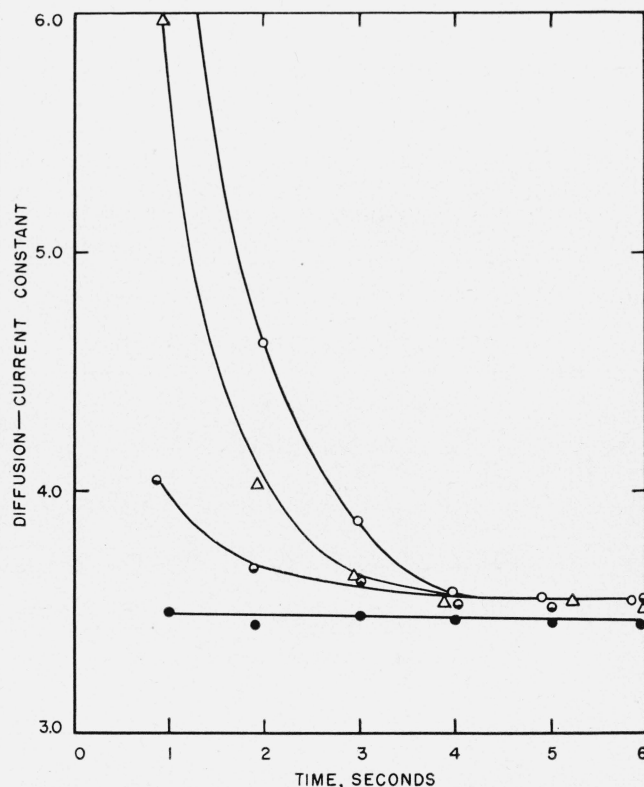


FIGURE 3. Diffusion-current constants obtained with marine barometer electrode.

Cadmium concentration ○=0.65 millimolar, no suppressor; △=1.60 millimolar, no suppressor; ◐=6.50 millimolar, no suppressor; ●=all above solutions, 0.01-percent gelatin.

0.1-*N* potassium-chloride -0.1-*N* hydrochloric-acid supporting electrolyte with a marine barometer tube capillary are plotted as a function of the drop-time of the electrode in figure 3. Diffusion-current measurements were made at an applied potential of -0.9 v, which is about 0.2 v more negative than the half-wave potential. For drop-times smaller than about 4 sec with no suppressor present, the diffusion-current constant shows a steady increase with decreasing drop-time, due to unsuppressed maxima. The effect is more pronounced for the most dilute solution. Apparently, maxima of about the same absolute value are present in each case that contribute a relatively larger amount to the total currents found for the dilute solutions. When 0.01 percent of gelatin was present, the three solutions gave values of *I* agreeing within ± 0.6 percent at each drop-time.

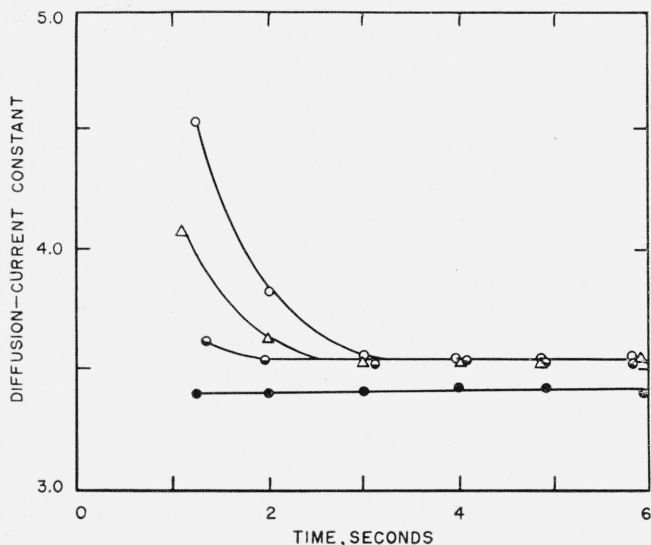


FIGURE 4. Diffusion-current constant obtained with electrode for which $mt=26$ mg.

Cadmium concentration $\circ=0.65$ millimolar, no suppressor; $\triangle=1.60$ millimolar, no suppressor; $\circ=6.50$ millimolar, no suppressor; \bullet =all above solutions, 0.01-percent gelatin.

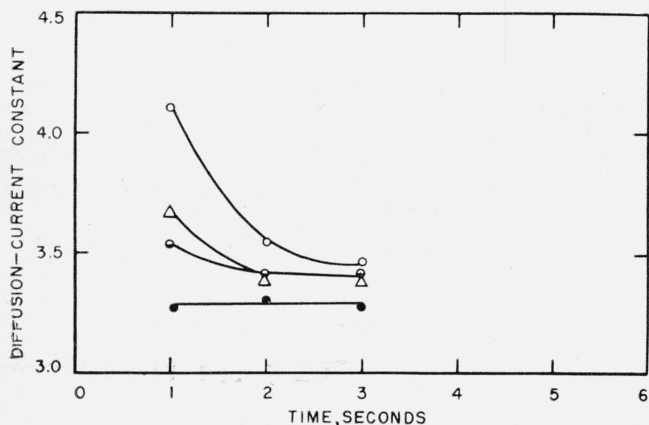


FIGURE 5. Diffusion-current constant obtained with electrode for which $mt=70$ mg.

Cadmium concentration $\circ=0.65$ millimolar, no suppressor; $\triangle=1.60$ millimolar, no suppressor; $\circ=6.50$ millimolar, no suppressor; \bullet =all above solutions, 0.01-percent gelatin.

The relation between the diffusion-current constant and the drop-time of the electrode, in the absence of suppressor, is dependent upon the size of the drop of the electrode. This is illustrated in figures 4 and 5, where data are shown for electrodes with drops having masses of 26 and 70 mg, respectively. It is evident that maxima are relatively less disturbing for the large-drop electrodes owing to the large limiting currents observed with them. The relatively constant values for *I* found in the presence of suppressor appear to decrease somewhat as the size of the drop is increased. This is being investigated further to determine whether it is due to a defect in the Ilkovic equation, which was used to correlate the experimental data.

For solutions containing no suppressor, the value of *I* will depend somewhat upon the potential at which the diffusion current is measured. At more negative potentials, for example, the values for drop-times less than 4 sec are somewhat smaller than those shown in figure 3. This is further illustrated in figure 6 for solutions of lead (0.5 millimolar) in the potassium-chloride-hydrochloric-acid medium. At the nominal values of the drop-time indicated at the right edge of the figure (accurate values of *t* were used in the computations), the

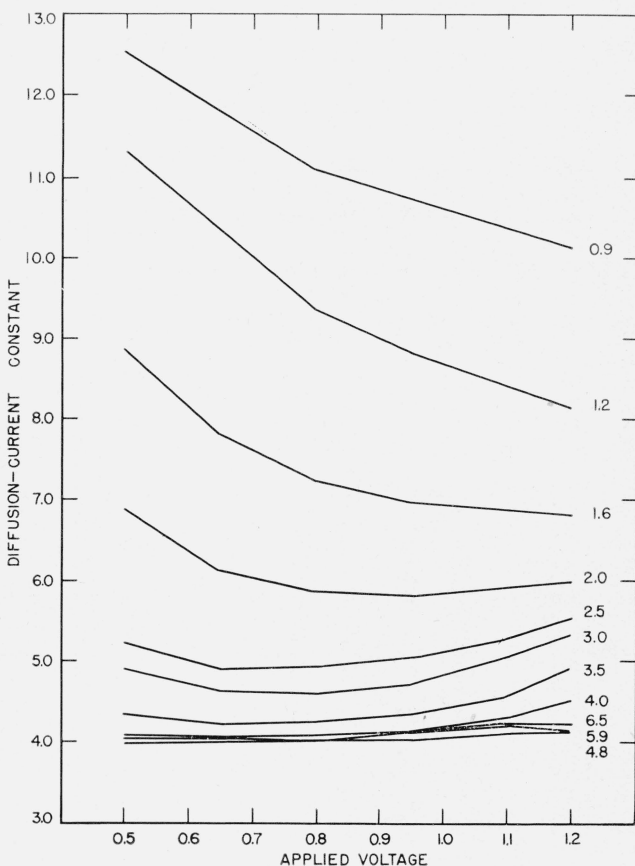


FIGURE 6. Dependence of the diffusion-current constant on the potential of measurement for various drop-times of the electrode in the absence of suppressor.

The numbers in the right edge of the figure indicate the nominal drop-time of the electrode.

values of I are plotted as a function of the voltage at which they were measured. Only for drop-times greater than 4 sec are any essentially constant values of I obtained. With suppressor present, however, the values of I are relatively insensitive to the potential at which they are measured, and this is one indication that the conditions in the solution are favorable for the evaluation of diffusion currents.

The effect of addition of gelatin to lead solutions is shown in figure 7. As the concentration of suppressor is increased, a longer range of drop-times for agreement between the several solutions is obtained. The drop-time below which the values of I increase rapidly has been designated "critical drop-time" in a previous paper [1], where it was shown to be a logarithmic function of the concentration of the suppressor. The slight increase of I with drop-time has also been found by other

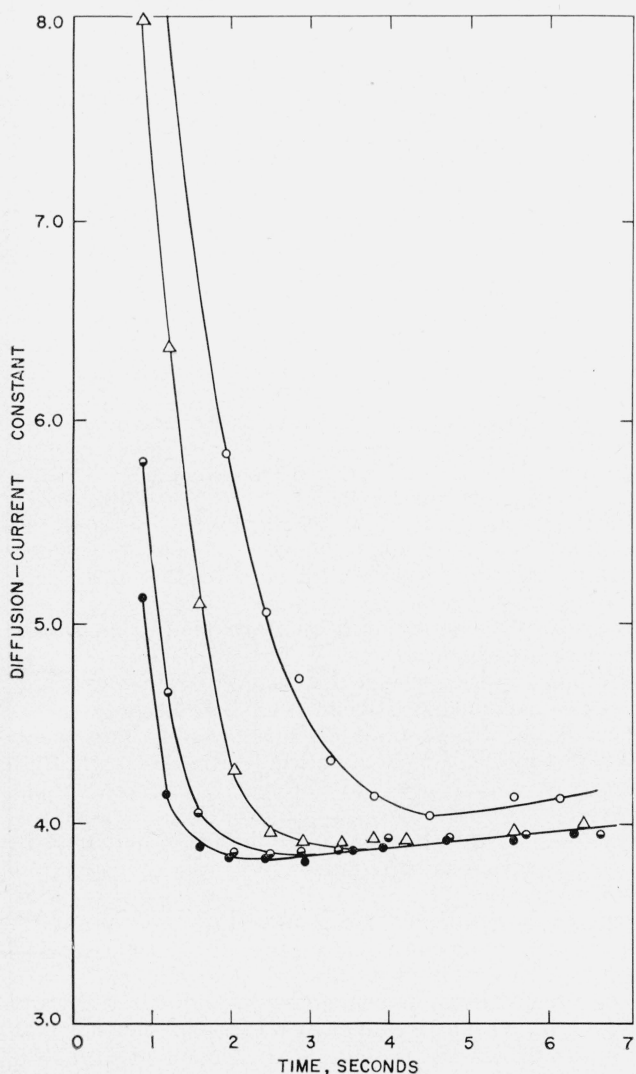


FIGURE 7. Effect of gelatin on the diffusion-current constant of lead.

Gelatin content: ○=none; △=0.002 percent; ◐=0.004 percent; ●=0.006 percent.

observers and is probably due to a defect in the Ilkovic equation.

Results obtained with methyl red as a suppressor are shown in figure 8. Although the behavior is similar to that found with gelatin, the small amount required for suppression of maxima should be noted.

Heyrovsky emphasizes that only small quantities of some suppressors are needed to suppress maxima and states that filtration of solutions through filter paper is all that is required in some cases [10]. This was confirmed and it was found that filtration of a lead solution through a Whatman paper was about as effective as adding 0.005-percent gelatin to the solution. Consequently, in these studies precautions were taken to reduce accidental impurities to a minimum by the use of unfiltered solutions, by special cleaning of the cells, and by the use of internal silver anodes. One impurity that

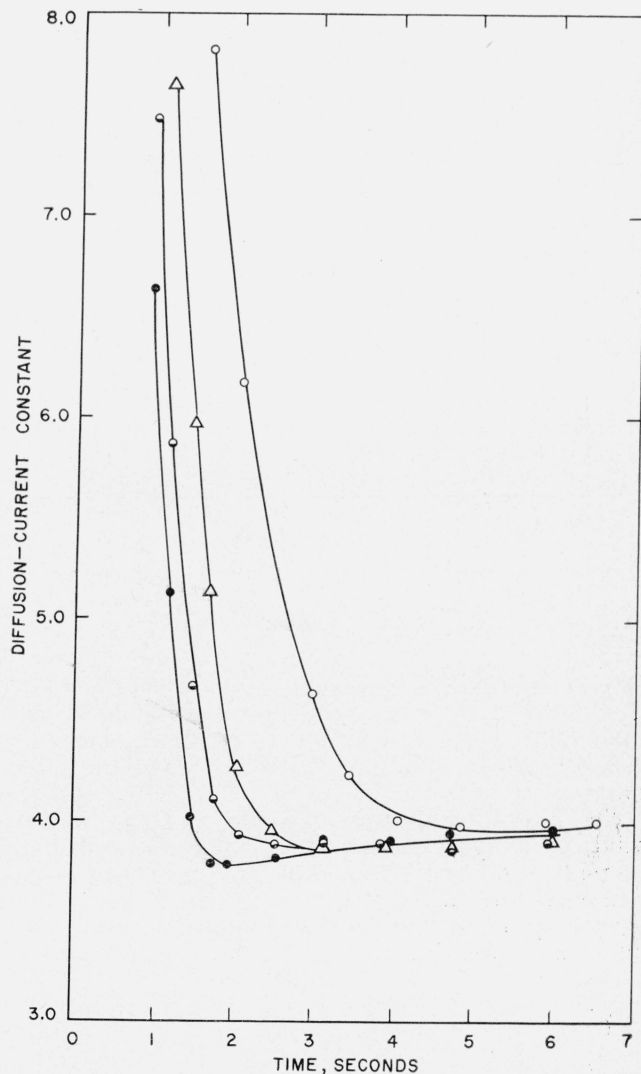


FIGURE 8. Effect of methyl red on the diffusion-current constant of lead.

Methyl red content: ○=none; △=0.0001 percent; ◐=0.0002 percent; ●=0.0003 percent.

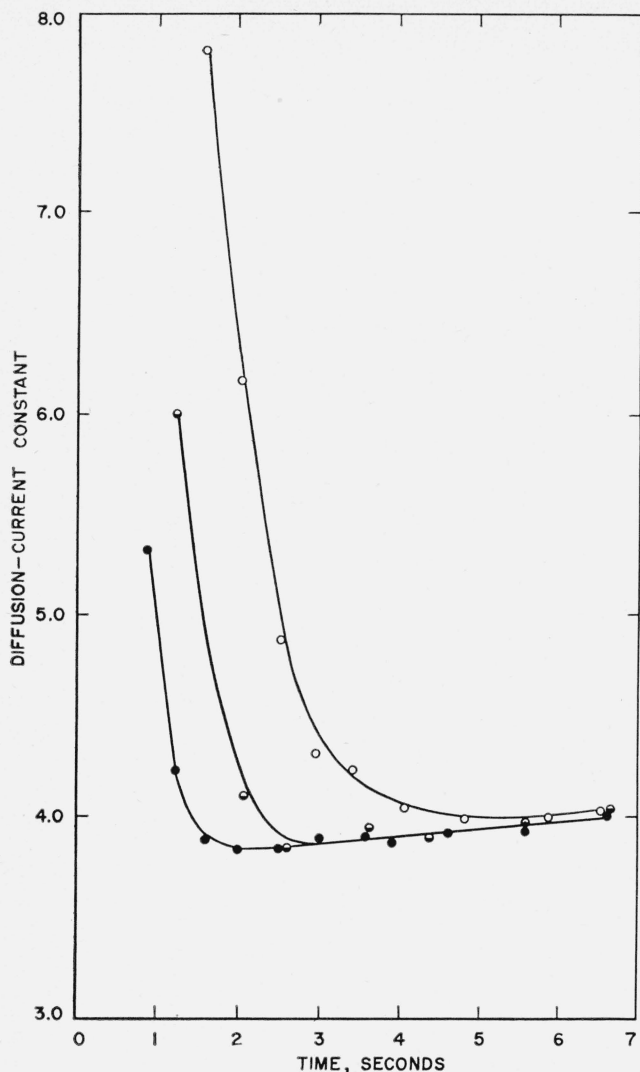


FIGURE 9. Effect of agar on the diffusion-current constant of lead.

Agar content: ○=none; ◐=0.0025 percent; ●=0.005 percent.

may enter solutions is dissolved agar when a plug of this material is used to minimize diffusion in the commonly used H-cell. The results shown in figure 9 indicate that agar is similar to gelatin in its suppressive action.

An experimental study was made of the rate of solution of agar and its effect upon the diffusion current. Solutions from which oxygen had been removed were introduced into an H-cell having an agar plug in the horizontal connecting arm, and diffusion-current measurements were made over a period of time. For a drop-time of 1.20 sec the diffusion current decreased slowly from an initially high value to a constant value after 2-hr contact of the solution with the plug. For drop-times of 1.70 and 2.40 sec, the times for attainment of constant values were 40 and 20 min, respectively. An experiment with a cell employing a fritted disk in the side arm for stabilizing the agar plug had

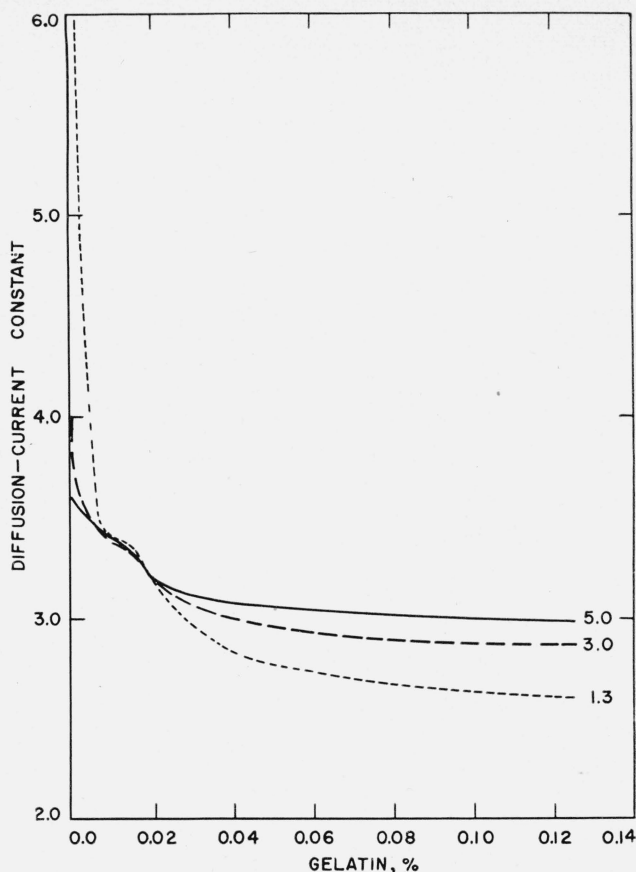


FIGURE 10. Effect of gelatin on the diffusion-current constant of cadmium.

The numbers at the right of the curves indicate the drop-time of the electrodes.

not reached equilibrium after 6-hr standing when the drop-time was 1.20 sec. As it is difficult to estimate the amount of agar that would dissolve from a plug in the side arm of a particular H-cell, any conclusions on the action of suppressors made from measurements with such an arrangement are open to question.

While suppressors are necessary to give essentially constant values of I over even a limited range of drop-times, one cannot indiscriminately add them to solutions. Indeed, it can be stated as a rule that anything added to a solution is with risk and should be done only after careful investigation of the consequences. The behavior of lead on addition of gelatin and its variation with the pH of the solution has been reported [11]. The effect of addition of large excesses of gelatin to cadmium solutions is shown in figure 10. Successive amounts of a concentrated solution of gelatin were added from a burette to a measured volume of cell solution, and, after stirring for 5 min. with a stream of nitrogen, diffusion-current measurements were made with the manual polarograph. Values of I were calculated, taking into consideration the resulting dilution of the solution. Results for a 0.65-millimolar solution of cadmium are shown, but data for 1.6- and 3.2-millimolar solu-

tions were comparable in all respects. Below about 0.006-percent gelatin the values of I are extremely sensitive to both the drop-time and the concentration of the suppressor. This corresponds to the region in which maxima are the controlling factors. From about 0.006- to 0.014-percent gelatin, the values are relatively insensitive to both drop-time and concentration of gelatin. In this region conditions are such that true diffusion currents are approximated. On further addition of gelatin, decreases in the diffusion current are observed, but the values for I increase with the drop-time of the electrode. Quantitative treatment of the results has not been successful as yet.

The data of figure 10 are plotted in figure 11 to show the variation of the diffusion-current constant with drop-time for a constant concentration of gelatin as suppressor. This figure supplements figure 10 and emphasizes the depressive action of large concentrations of gelatin.

The effects of bovine albumin and of sodium carb-

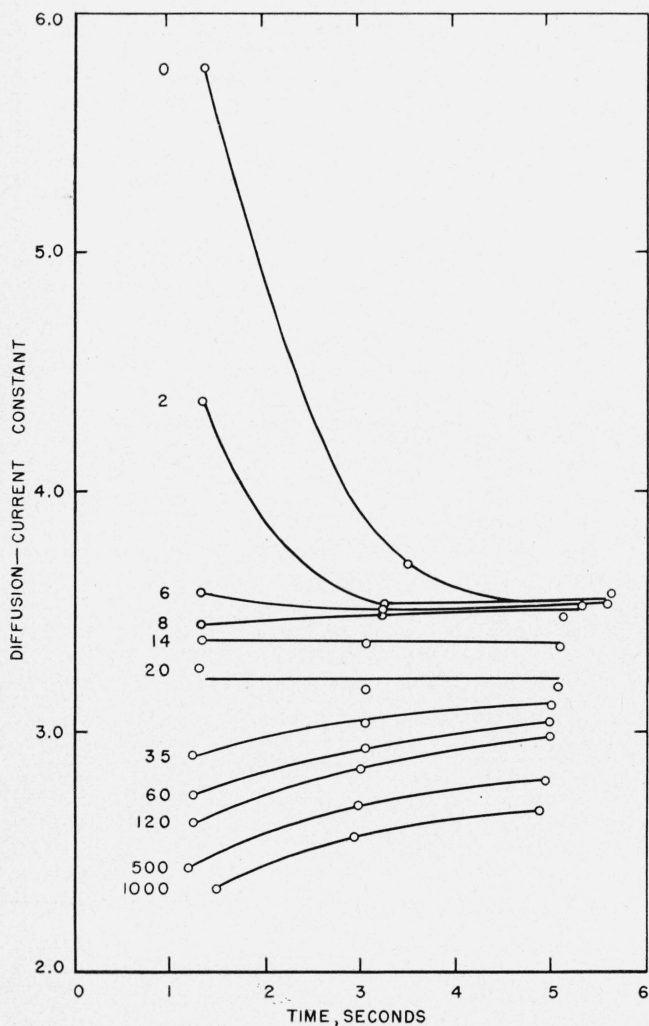


FIGURE 11. Dependence of the diffusion-current constant of cadmium on the drop-time in the presence of gelatin.

The numbers to the left of the curves indicate the gelatin content in thousandths of percent.

oxymethylcellulose [11] on the diffusion current of cadmium are shown in figures 12 and 13, respectively. Additions of small amounts of these materials are sufficient to suppress maxima, whereas large amounts depress the diffusion current, especially at the low drop-times. The depressive effect is much less, however, than in the case of gelatin.

4. Discussion

The results presented above are typical of the many obtained at the Bureau. Ions studied have included thallium, lead, bismuth, cadmium, nickel, and cobalt. In all cases, abnormally large values have been obtained for the limiting current in the absence of some suppressor, whether or not deformations of the wave shapes in the form of readily recognizable maxima are present.

It is difficult to make quantitative statements about the minimum amounts of suppressor that are necessary to eliminate maxima. The occurrence of maxima is so general that it is doubtful if any polarographic measurements made with pure solutions are entirely free from their influence. Small amounts of impurities of a surface-active nature are often unintentionally or unknowingly present in solutions, so that polarographically pure solutions may not always be realized. It is shown that extremely small amounts of some suppressors are sufficient to suppress maxima and that even a simple filtration

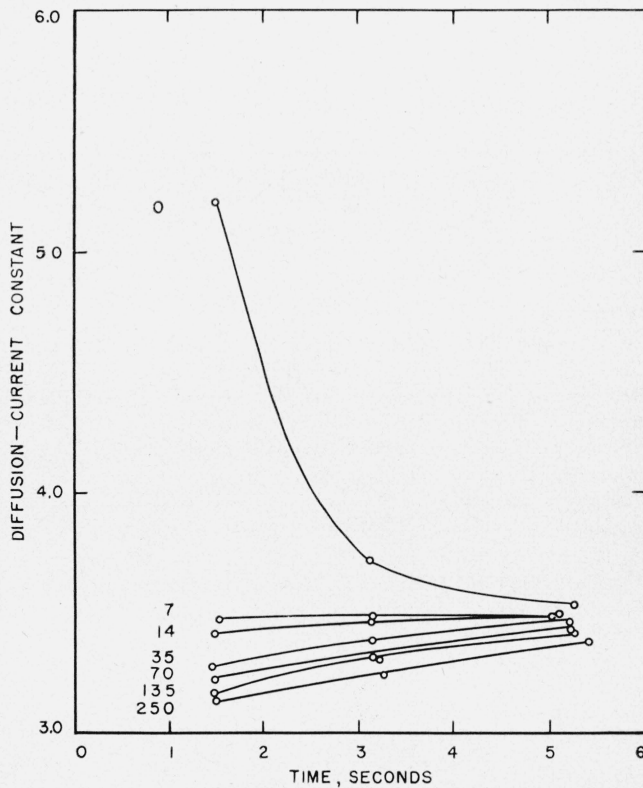


FIGURE 12. Dependence of the diffusion-current constant of cadmium on the drop-time in the presence of bovine albumin.

The numbers to the left of the curves indicate the albumin content in thousandths of percent.

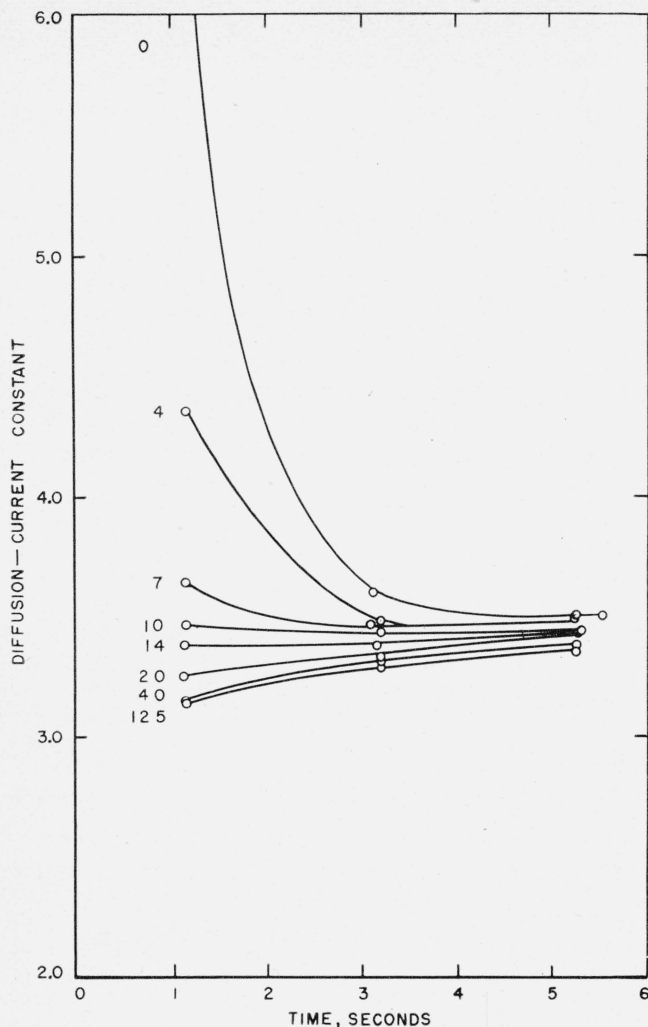


FIGURE 13. Dependence of the diffusion-current constant of cadmium on the drop-time in the presence of sodium carboxymethylcellulose (NaCMC).

The numbers to the left of the curves indicate the NaCMC content in thousandths of percent.

through paper produces marked changes in the behavior of the solution. Small amounts of insoluble material, such as wood chips, occasionally found in chemical reagents may have an unpredictable influence on the diffusion current.

Large excesses of suppressors have depressive action on polarographic diffusion currents. As a result, one cannot indiscriminately add materials to solutions in the hopes of reducing maxima to negligible proportions. In any measurements in which

true diffusion currents are required, it is necessary for the experimenter to establish not only that the electrode reaction is limited solely by the rate of diffusion, but the chemical nature of the electrolyzed material must also be known.

There appear to be two criteria for the establishment of diffusion as the rate-controlling process at the electrode. One is the independence of the current (after correction for the residual current) with the voltage at which it is measured. In other words, a diffusion current plateau should exist beginning at the completion of the wave and continuing with increasing potential until the onset of a second electrode reaction. The second criterion is concerned with the dependence of the current upon the dropping rate of the electrode. This is difficult to apply because the theoretical dependence has not been definitely established. The Ilkovic equation has been used for this purpose, and linear dependence of the diffusion current upon the square root of the pressure of the mercury column or independence of the diffusion-current constant with drop-time of the electrode have been the criteria employed. Recent theoretical and experimental work has shown that the Ilkovic equation is an approximation and that systematic errors of several percent can be expected with electrodes of the size normally used in polarographic measurements. In applying the second criterion for diffusion control, the modified forms of the equation should be used, or the Ilkovic equation may be used if its defect is taken into consideration. In any case, the experimental conditions and composition of the solution should be varied in both directions to establish that a critical state does not exist.

5. References

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