Amperometric Titration of Potassium with Sodium Dipicrylaminate

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Amperometric titration of potassium with sodium dipicrylaminate has been studied by B. Sandberg⁽¹⁾ and A. Langer *et al.*,⁽²⁾ but the details are not given. In the present paper

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(1) B. Sandberg, *Svensk. Kem. Tid.*, **58**, 197 (1946); *C. A.*, **41**, 349 (1947).

(2) A. Langer and D. P. Stevenson, *Ind. Eng. Chem., Anal. Ed.*, **14**, 770 (1942).

the analytical procedure is shown and the results are discussed.

Experimental

Chemicals and Apparatus Used.—Sodium Dipicrylaminate was Hexyl Natrium made by Nippon Kasei Chemical Industries Limited. The polarograph used by the author was a Heyrovsky-Shikata type made by Yanagimoto Co., Kyoto. For amperometric titration both the portable electronic instrument of Delahay's type(3) and the arrangement as shown in Fig. 1 were used.

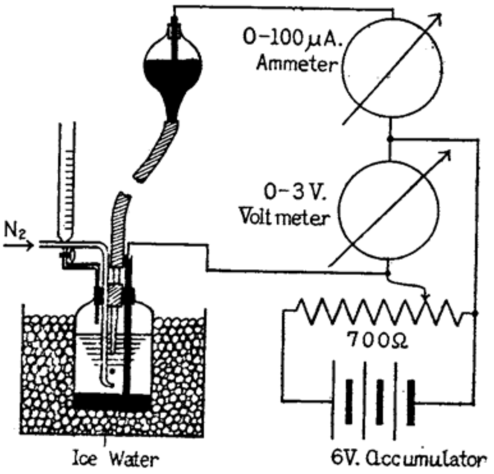

Fig. 1.

Polarographic Behavior of Sodium Dipicrylaminate.—A polarogram of sodium dipicrylaminate in Palitzsch's borate buffer solution (pH 8.98) is shown in Fig. 2. Three waves were obtained, the first small, the second obscure and the third was a large wave with maximum. The wave-height of the first was not proportional to the concentration of dipicrylaminate. The maximum in the third wave was not suppressed by gelatin, but the diffusion currents of dipicrylaminate in the above mentioned buffer solution at −1.60 V. applied *vs.* mercury pool were proportional to its concentration smaller than 3×10^{-3}.

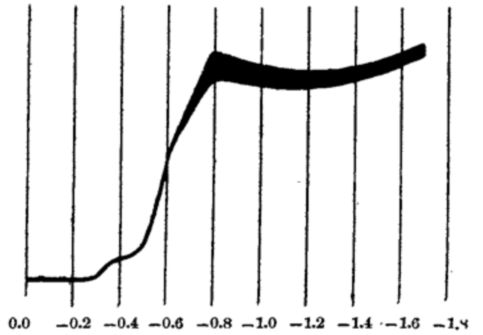

Fig. 2.—A polarogram of sodium dipicrylaminate in Palitzsch's borax buffer solution (pH 8.98): Sensitivity, 1/100; concentration, 16.4 $\times10^{-5}$; anode, Hg-pool.

Procedure.—A measured volume of the sample was introduced into the cell, neutralized with sodium hydroxide and 50 ml. of the buffer solution were added. After passing nitrogen gas for ten minutes and cooling in an icewater-bath, the −1.60 V. *vs.* mercury pool was applied to the cell and the current was measured. N/10 sodium dipicrylaminate solution was added successively with a microburette. After each addition the content in the cell was mixed by passing nitrogen gas for ten minutes and the current was recorded. During the titration, the electrolyte must be cooled in an icewater-bath at 0° −2°. In all cases the values of the current, corrected for the volume change, were plotted against the amount of reagent added.

Results

Results obtained in the titration are given

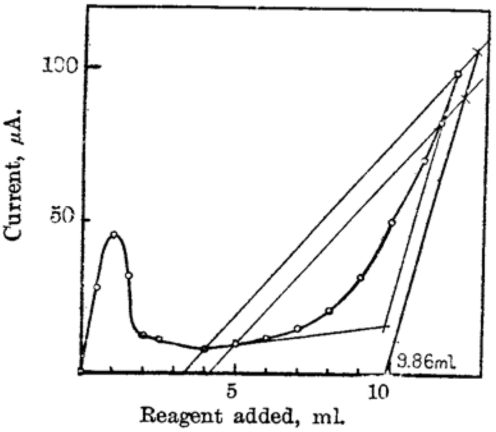

Fig. 3.—Titration curve of sample No. 1.

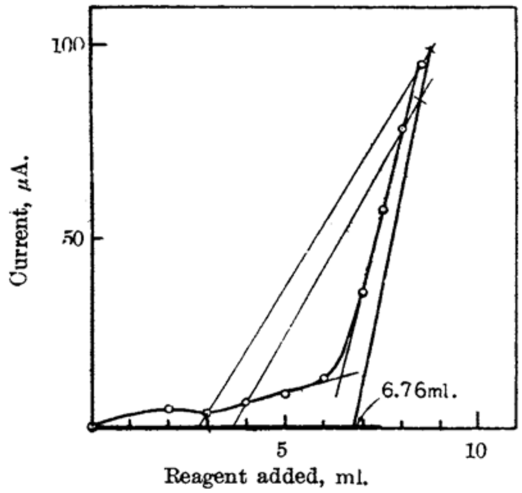

Fig. 4.—Titration curve of sample No. 2.

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(3) P. Delahay, *Anal. Chem.*, **21**, 1425 (1949).

in Table 1 (Figs. 3, 4, 5, 6, 7, 8 and 9). The point obtained by the intersection of the tangents became different from the point obtained by the intersection of the asymptotes of titration curve according to Langer *et al.* When the end-point was located on the point obtained by the intersection of the asymptotes, the results obtained showed coincidence with that calculated. At the beginning of titrations supersaturation was held, so that when there was no more than 30 mg. K, the portion of the titration curve before the end-point was not complete enough to obtain an asymptote. The presence of 350 mg. Na did not interfere and in presence of aluminate and precipitate of ferric hydroxide the titration was not affected.

Table 1

Sample No.	Used, mg.	End-point obtained, ml.	K found, mg.
1	K 39.1 Na 17.3	9.86 (9.80)	39.1 (38.9)
2	K 27.6 Na 17.3	6.76 (6.49)	26.8 (25.8)
3	K 72.7 Na 17.3	18.36 (16.97)	72.9 (67.4)
4	K 52.2 Na 412.6	13.18 (12.67)	52.3 (50.3)
5	K 26.4 Na 412.6	6.31	25.0
6	K 34.7 Na 336.4	8.68	34.5
7	K 51.4 Na 17.3 Fe 43.2 Al 22.3	12.97 (12.28)	51.5 (48.8)

The values obtained by the intersection of tangents were given in brackets. No. 7 was titrated, using a microammeter of 100 microamperes in full scale.

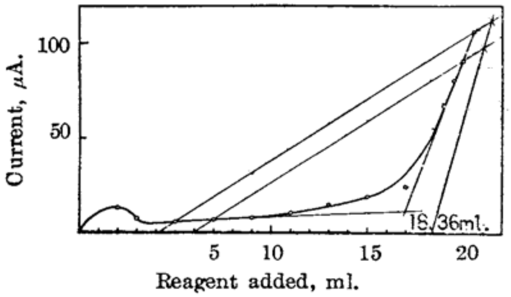

Fig. 5.—Titration curve of sample No. 3.

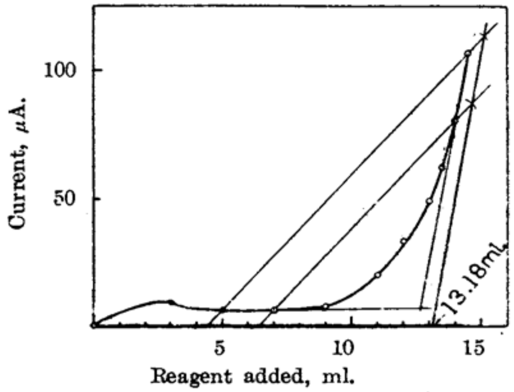

Fig. 6.—Titration curve of sample No. 4.

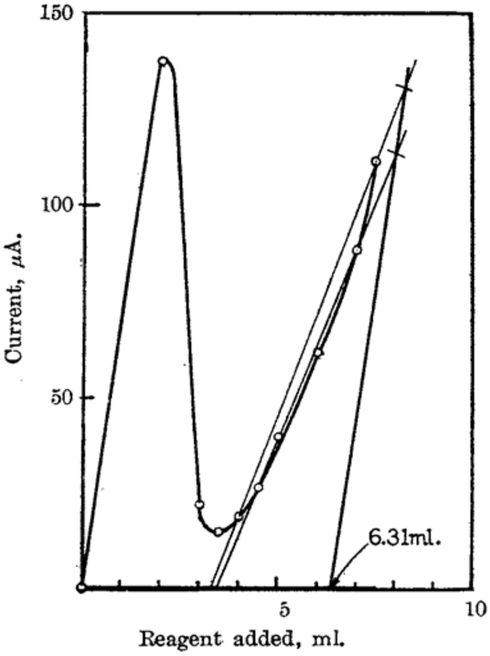

Fig. 7.—Titration curve of sample No. 5.

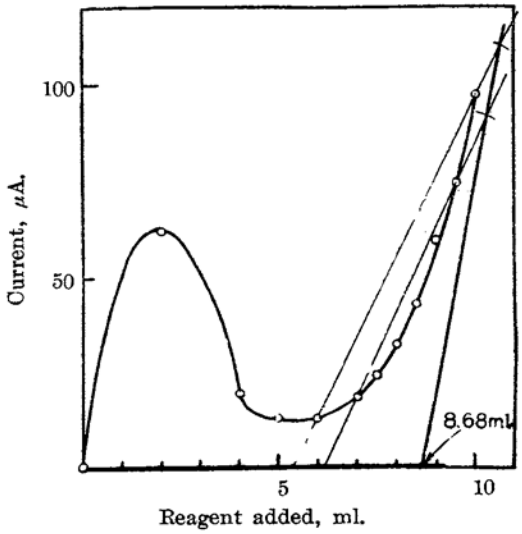

Fig. 8.—Titration curve of sample No. 6.

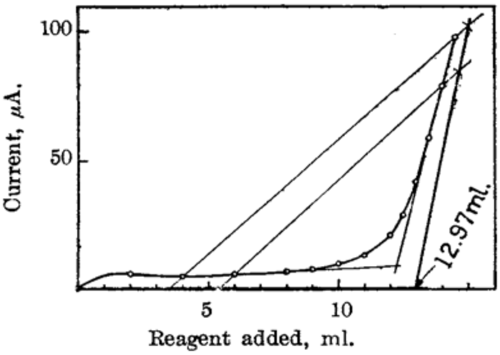

Fig. 9.—Titration curve of sample No. 7 (A 100-microammeter was used).

The great diffusion current of dipicrylaminate made a microammeter of 100 microamperes in full scale useful instead of a galvanometer.

Discussion

Mercury pool was used for the anode, for the reason that if calomel electrode was used, potassium ion might stray into the cell and that the diffusion current of dipicrylaminate was so great that the potential drop through the connecting bridge would not be negligible. Applied potential should be changed with the composition of sample. When the sample was chloride, −1.60 V. was applicable. Although dipicrylaminate seemed to be not completely dissociated, in the present work the end point was located negleting the undissociated dipicrylaminate.

Summary

In the amperometric titration of potassium with dipicrylaminate, the end-point located by the theory of Langer *et al.* showed satisfactory results. The accuracy was within 1 mg. with more than 30 mg. K. In presence of 350 mg. Na, or aluminate and precipitate of ferric hydroxide the titration was not affected.

In conclusion the author wishes to express his sincere thanks to Mr. S. Sato in this laboratory for his kind advice.

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