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# Quantitative Polarographic Determination of Aliphatic Esters

TH. ØSTERUD and MILDA PRYTZ

*Yrkeshygienisk Institutt, Blindern — Oslo, Norway*

Reaction mixtures of pure aliphatic esters with hydroxylamine have been polarographed at well defined concentrations in ethanol-water solutions of tetrabutylammonium iodide, buffered with tetraethylammonium hydroxide. The height of the resulting hydroxamic acid curves show proportionality with the original concentration of ester.

A series of esters were treated with hydroxylamine in alcoholic sodium hydroxide solutions as described in our paper on polarographic reduction of aliphatic esters [1]. After the addition of the hydroxyl amine solution the concentration of ester in the reaction mixture was 0.031 M. The supporting electrolyte had a pH of about 12.5. To 10 ml of the supporting electrolyte in the electrolytic cell was added respectively 5, 10, and 15 drops of the reaction mixture. This gave for the acetic acid ethyl ester (ethyl ethanoate) the concentrations $3.1 \times 10^{-4}$ M, $6.2 \times 10^{-4}$ M and $9.3 \times 10^{-4}$ M. The molar concentrations of the other esters were of the same order of magnitude.

The solutions were polarographed, and the height of the polarographic waves (steps) was found to vary proportionally with the amount of ester. When the concentration of ester was doubled the height of the corresponding wave became twice as large as originally.

## EXPERIMENTAL

The same apparatus was used as in our earlier study [1]. The experimental procedure was similar to that already described and the chemicals used were the same. To 10 ml of supporting electrolyte in the electrolytic cell was added, respectively, 5 drops, 10 drops, and 15 drops of the reaction mixture and the pH was kept at approximately 12.5. 5 drops or 10 drops of the reaction mixture were weighed and the molarity of the polarographed solutions calculated accordingly. They were of the order of magnitude of $10^{-4}$ M. After addition of, respectively, 5 and 10 drops (molar concentrations $3.1 \times 10^{-4}$ to $6.2 \times 10^{-4}$) the waves were quite regular with very good, measurable plateaus. On addition of 15 drops of reaction mixture, however, the resulting third wave was apt to show a maximum. This might have been due either to the higher concentration or to the solution having been polarographed twice already. We therefore added 15 drops of reaction mixture directly to 10 ml of supporting electrolyte and polarographed in the usual way. Also by this method we got an ill-defined plateau. As to be expected the halfwave

potentials were not influenced by concentration; the same values were obtained as given in the above mentioned paper [1]. It seems practical for quantitative purposes not to exceed a concentration of $6 \times 10^{-4}$ M in order to evade plateaus with maxima. By all these experiments we used a sensitivity of 7:1 000.

In order to test the usability of an ester solution with known concentration in comparison with an ester solution of unknown concentration we ran some parallels. In one case we heated two reaction mixtures with the same amount of ester similtaneously in the same waterbath and polarographed both at room temperature. The waves were of equal height. In another case one of the reaction mixtures contained one and a half as much ester as the other. The wave heights varied according to concentration.

One has to keep in mind that the reaction between ester and hydroxylamine is reversible, and one should always treat an ester solution of known strength and the one of unknown concentration identically in every detail if one wishes to measure the concentration of the latter by comparison with the former.

## RESULTS

Firstly we tested the variation of wave heights with concentration by adding increasing amounts of one and the same reaction mixture to an electrolytic cell with 10 ml of the above mentioned supporting electrolyte. Seven different aliphatic esters have been treated in this way. These experiments showed that the wave heights increased proportionally with the concentration within the limits $\pm$ 5 %. The results are given in Table 1.

Fig. 1. gives the diagram for acetic acid *iso*propyl ester.

We also found it important to ascertain if two different reaction mixtures of equal concentration gave equally high waves when treated under exactly similar conditions. The result was satisfactory as shown in Fig. 2. Two different reaction mixtures with acetic acid *iso*propyl ester show exactly the same shape of curve and have the same wave height.

Eventually we found it expedient to test if the proportionality between concentration and wave height which had been found when we added increasing amounts of a reaction mixture to one and the same polarographic cell would be evident if we added increasing amounts of reaction mixture (4 and 6

*Table 1.* Relationship between concentration and wave height in polarographic determination of aliphatic esters.

| Ester | Mol. conc. × $10^{-4}$ | | | Relative concentration | | | Wave heights in mm | | | Relative heights measured | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| Acetic acid ethyl ester | 3.1 | 6.2 | 9.3 | 1 | 2 | 3 | 27 | 55 | 81 | 1 | 1.9 | 3 |
| Acetic acid *iso*propyl ester | 3.1 | 6.2 | 9.3 | 1 | 2 | 3 | 23 | 43 | 68 | 1 | 2 | 3 |
| Acetic acid octyl ester | 3.1 | 6.2 | 9.3 | 1 | 2 | 3 | 24 | 47 | 74 | 1 | 2 | 3.1 |
| Propionic acid ethyl ester | 3.1 | 6.2 | 9.3 | 1 | 2 | 3 | 23 | 45 | 72 | 1 | 2 | 3.1 |
| Butyric acid ethyl ester | 3.1 | 6.2 | 9.3 | 1 | 2 | 3 | 27 | 54 | 79 | 1 | 2 | 2.9 |
| Butyric acid butyl ester | 3.1 | 6.2 | 9.3 | 1 | 2 | 3 | 26 | 54 | 78 | 1 | 2.1 | 3 |
| Valeric acid ethyl ester | 3.1 | 6.2 | 9.3 | 1 | 2 | 3 | 23 | 45 | 68 | 1 | 2 | 3 |

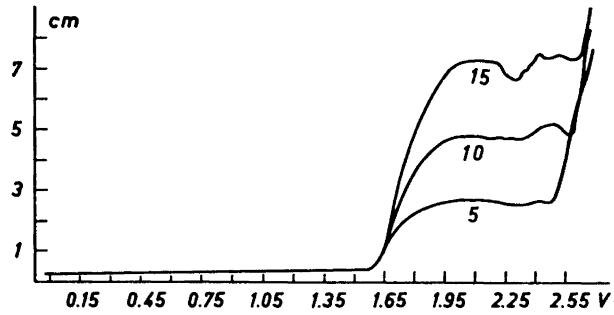


*Fig. 1.* Variation of wave height with concentration for acetic acid *iso*propyl ester. Concentrations: 3.1, 6.2 and 9.3 × $10^{-4}$ M.

drops, respectively) to different cells, each with 10 ml of supporting electrolyte. The results for acetic acid *iso*propyl ester are shown in Fig. 3. The figure shows that also with this procedure we got proportionality.

## DISCUSSION

We presume to have shown that our method for indication of aliphatic esters by conversion to hydroxamic acid and polarographic determination of the reaction mixture also may be used for quantitative determination of the same. The results are reliable within the limits of ± 10 %.

One must always keep in mind that the reaction

$$\text{ester} + \text{hydroxylamine} \rightleftharpoons \text{hydroxamic acid} + \text{alcohol}$$

is reversible, so that reaction mixtures for quantitative use must be made very carefully. Comparisons between different reaction mixtures are only allowed when these have been prepared under exactly similar conditions.

Water solutions with alkali salts as supporting electrolyte can not be used, because of the high decomposition potentials of the hydroxamic acids.

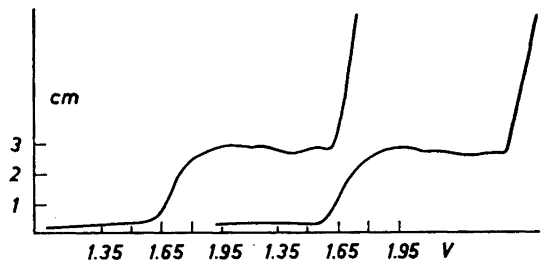


*Fig. 2.* Polarographic waves for two different reaction mixtures similarly treated, showing the same wave height. Conc. of acetic acid *iso*propyl ester: 3.1 × $10^{-4}$ M.

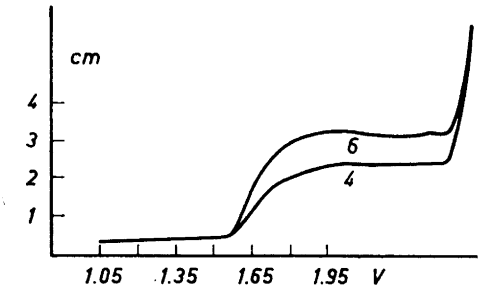


*Fig. 3.* Polarographic waves of acetic acid *iso*propyl ester showing proportionality between concentration and wave height even when different electrolytic cells were used. Concentrations: 2.5 and 3.7 $\times$ $10^{-4}$ M.

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## REFERENCE

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