Interaction of (+)-Tartrate with Methanediol in Alkaline Solutions

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The equilibrium of acetal-type compound formation from (+)-tartrate and methanediol in alkaline solutions has been studied and characterized quantitatively.

The ability of formaldehyde to oxidize on Hg has been detected recently and (+)-tartrate [(2*R*,3*R*)-tartrate] has been shown to have a retarding effect on the oxidation process.[4] Mixed Cu^{II} complexes with tartrate and formaldehyde have been shown to form in some cases.[5]

Formaldehyde is known to exist largely in hydrated form in solution ($K_e = 2 \times 10^3$):[6]

$$HCHO + H_2O \rightleftharpoons H_2C(OH)_2 \quad (1)$$

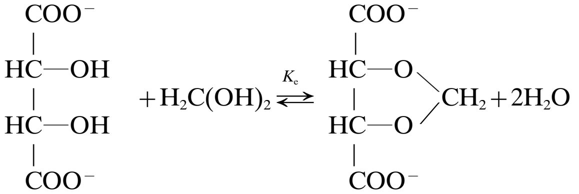
The dissociation of methanediol takes place in alkaline soltuions ($pK_a \sim 13$[7]):

$$H_2C(OH)_2 \rightleftharpoons H_2C(OH)O^- + H^+ \quad (2)$$

The limiting current of methanediol oxidation on a dropping mercury electrode (DME) is diffusion limited. The values of i_{lim} do not depend on solution pH in the range 13.2–13.7 (0.1–0.6 mol dm^{-3} NaOH) (curve 1, Fig. 2). The decrease in i_{lim} in more alkaline solutions (pH > 13.7) is related to increase in solution viscosity.

The addition of tartrate into alkaline methanediol solutions at pH 13.0–14.0 diminishes the i_{lim} (curve 2, Fig. 2). The results obtained can be explained by binding of a part of the methanediol to an electrochemically non-active compound which does not take part in the anodic oxidation process.

On the basis of polarographic data a reaction for the formation of an acetal-type compound from methanediol and tartrate anion is proposed:



$$\begin{array}{c} COO^- \\ | \\ HC-OH \\ | \\ HC-OH \\ | \\ COO^- \end{array} + H_2C(OH)_2 \overset{K_e}{\rightleftharpoons} \begin{array}{c} COO^- \\ | \\ HC-O \\ | \\ HC-O \\ | \\ COO^- \end{array} \rangle CH_2 + 2H_2O \quad (3)$$

The equilibrium constant K_e of reaction (3) was calculated from polarographic data (values of i_{lim}), assuming that i_{lim} is proportional to the methanediol concentration in solution and that equilibrium (3) is rather slow (acetal does not dissociate additionally in the polarographic oxidation process). The dissociation of one tartrate anion OH$^-$ group was taken in account ($pK_{a_3} = 14.3$[8]):

$$C_4O_6H_4^{2-}(T^{2-}) \rightleftharpoons C_4O_6H_3^{3-}(T^{3-}) + H^+ \quad (4)$$

The results obtained show good agreement between the calculated log K_e values over the total pH range investigated, with the equilibrium of reaction (3) being shifted to the left ($\log K_e = -0.8 \pm 0.1$).

The results obtained were confirmed using ^{1}H NMR techniques. The ^{1}H NMR spectra of formaldehyde in a D_2O solution were recorded over the pH range 10–14. At pH 10, in addition to the solvent signal, the NMR spectrum exhibits a single signal for the methylene protons of the hydrated form of formaldehyde at δ 4.88. At pH 14 a single peak is observed at δ 4.90. The chemical shift difference between these two lines is small, *ca.* δ 0.02, as should be expected since the magnetic environments of methanediol and its anion are very similar. The spectra observed may be explained by the dissociation reaction (2) and a weighted average of the two forms of methanediol is detected by NMR. Intensity measurements are inaccurate because the signals fall on the side of the strong water signal.

The ^{1}H NMR spectrum of the tartrate solution in D_2O shows a single peak at δ 4.35 for the protons adjacent to the hydroxy groups over the range of pH values studied.

The mixtures of the solutions discussed above using various molar ratios of the compounds, *i.e.* tartrate–CH_2O 10:1, 1:1 and 1:2, were studied over the pH range 10–14, the NMR spectra being recorded at appropriate time intervals. The ^{1}H NMR spectra recorded within a few minutes after making up of the solutions displayed signals corresponding to the individual components of the mixture with the shift values discussed above. However, after a 10–20 min period (this corresponds to the procedure used for polarographic measurements) new signals at δ 5.16 and 4.62 could be detected. The shape of the signals indicates an interaction between the tartrate and the methanediol, resulting in the formation of the symmetrical structure as shown in eqn. (3). The singlet at δ 5.16 is about 10% of the intensity of the methylene signal of methanediol and was assigned to the formation of an acetal-type compound [eqn. (3)]. The signal for the methylene protons is displaced downfield compared to that for hydrated acetals,[9] and this can be explained by the non-customary acetal structure of this compound. This signal is observed also after the mixture was kept at room tempera-

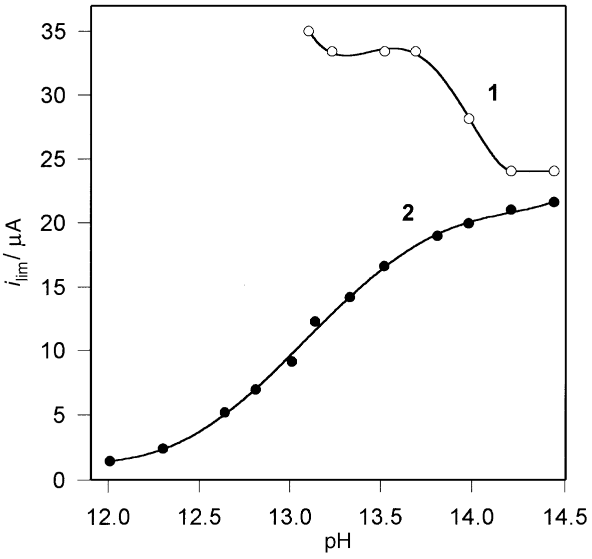


Fig. 2 Dependence of the limiting current of methanediol oxidation on a DME on the solution pH: *solution composition*: 1, 3.2 mmol dm^{-3} methanediol + NaOH; 2, 3.2 mmol dm^{-3} methanediol + 40 mmol dm^{-3} (+)-tartrate + NaOH

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ture for several days, although the intensity of the methylene signal of methanediol decreases significantly over this period owing to the Cannizzaro reaction. Peaks at δ 3.35 and 8.46 are observed after 30 min of mixing the solutions and correspond to the methyl group of methanol and the methylene proton of formate ion, respectively. These signals increase significantly after longer reaction periods and ultimately the methylene signal of the methanediol is of the same intensity as the proton signal of the formate ion.

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Techniques used: DC-polarography, ^{1}H NMR

References: 9

Fig. 1: Polarographic calibration graph

Fig. 3: ^{1}H NMR spectrum of (+)-tartrate–methanediol mixture at pH 13 after 20 min

Fig. 4: ^{1}H NMR spectrum of (+)-tartrate–methanediol mixture at pH 13 after 12 h

Table 1: Equilibria concentrations of reacting species and calculated values of log K_e of reaction (3)

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References cited in this synopsis

4 A. Vaškelis and E. Norkus, *J. Electroanal. Chem.*, 1991, **318**, 373.
5 A. Vaškelis, E. Norkus and I. Žakaitė, *Galvanotechnik* in press.
6 L. F. Roeleveld, J. M. Los and B. J. C. Wetsema, *J. Electroanal. Chem.*, 1975, **75**, 819.
7 R. Schumacher, J. J. Pesek and O. R. Melroy, *J. Phys. Chem.*, 1985, **89**, 4338.
8 E. P. Serjeant and B. Dempsey, *Ionisation Constants of Organic Acids in Aqueous Solutions*, Pergamon, Oxford, 1979.
9 P. Greenzaid, Z. Luz and D. Samuel, *J. Am. Chem. Soc.*, 1967, **89**, 749.