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Influence of Ionic Strength and Cation Nature on the Deprotonation of Methanediol in Alkaline Solution†

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The pK_a values of methanediol deprotonation were found to decrease with increase in solution ionic strength as estimated by a ^{13}C NMR titration method.

Formaldehyde is hydrated in aqueous solutions forming methanediol:

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

The equilibrium constant of reaction (1) was found to be 2×10^3 [1] and 2.3×10^3.[2,3] This suggests that nearly all formaldehyde is present in hydrated form in aqueous solutions. In alkaline aqueous solutions dissociation (deprotonation) of methanediol occurs:[4]

$$H_2C(OH)_2 \overset{K_a}{\rightleftharpoons} H_2C(OH)O^- + H^+ \qquad (2)$$

or

$$H_2C(OH)_2 + OH^- \rightleftharpoons H_2C(OH)O^- + H_2O \qquad (3)$$

Methanediol and its anion are assumed to be of different activity in various reactions, *e.g.* methanediol anion rather than methanediol is thought to participate in anodic oxidation of formaldehyde in alkaline solutions.[5–10] However, methanediol is an active species during the interaction with tartrate.[11] Therefore it is important to know the exact value of the deprotonation constant (pK_a) of methanediol.

Different values of methanediol deprotonation constants (pK_a from 12.5 to 13.6 at 20–25 °C) were obtained using various experimental techniques: 12.5 (spectrophotometry),[12] 13.1 (^{13}C NMR),[7] 13.3 (conductometry)[13] 13.4[2] and 13.6 (polarography).[14] The scatter in the available pK_a values can be attributed to the different ionic strengths of the solutions investigated. Therefore the aim of this work was to determine the influence of ionic strength on methanediol deprotonation. The systems investigated were: CH_2O–KOD–KNO_3–D_2O, CH_2O–$NaOD$–$NaNO_3$–D_2O and CH_2O–$LiOD$–$LiNO_3$–D_2O.

Results and Discussion

To study the equilibrium between methanediol and its anion form we have used ^{13}C NMR spectroscopy. Various NMR techniques can be used, *e.g.* ^{1}H, however the latter method is not very accurate since the difference of the chemical shift between two forms in some solutions does not exceed 0.1 ppm.[15]

The ^{13}C spectra were measured in formaldehyde solutions (0.38 mol dm^{-3}) at the ionic strength (I) of the electrolyte, 0.4 and 1.0 mol dm^{-3}. Formaldehyde solutions in water are known to form polyoxymethylene glycols of various compositions and molecular weights.[4] In this work we studied alkaline solutions of formaldehyde prepared by dissolving trioxymethylene in supporting electrolyte solutions. The low concentration of formaldehyde was used to avoid oligomer formation and no signals of the oligomeric forms of formaldehyde were observed in the NMR spectra under these conditions. Owing to the rapid proton exchange between methanediol and its anion a single ^{13}C signal which is the weighted average of the shift of both species is observed in the spectrum. The chemical shift (δ) of the protonated form of methanediol is observed at 83.0 ppm in accordance with literature data.[16] The chemical shift was measured relative to the methylene and methyl carbon lines of ethanol as a reference compound by addition of *ca.* 10%

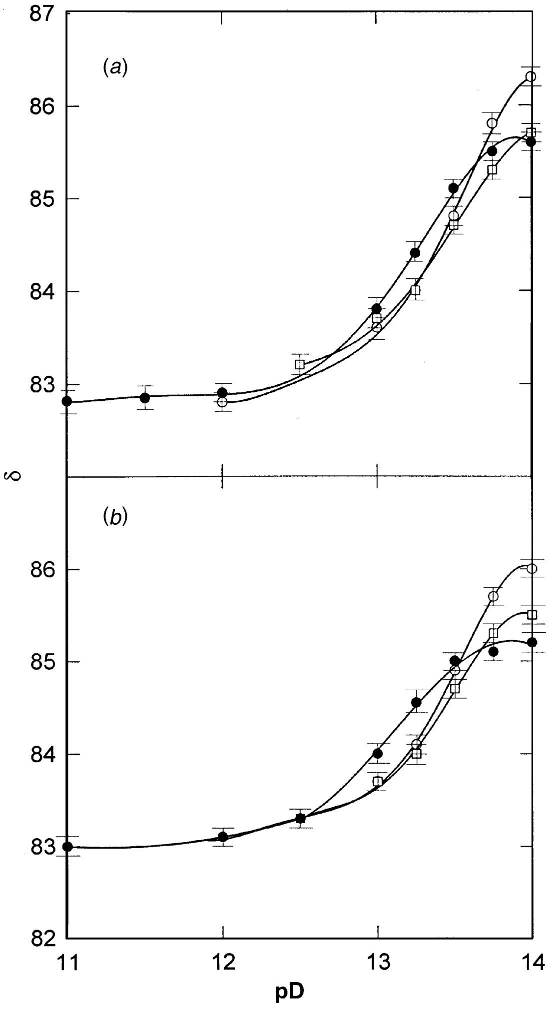

Fig. 1 The ^{13}C chemical shift of methanediol *vs.* pD at 25 °C $[CH_2O] = 0.38$ mol dm^{-3} I/mol dm^{-3} = 0.4 (*a*), 1.0 (*b*). ○, $LiOD + LiNO_3$; ●, $NaOD + NaNO_3$; □, $KOD + KNO_3$

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Table 1 Dependence of methanediol pK_a values (calculated from ^{13}C NMR data) on the ionic strength of solution at 25 °C

I/mol dm^{-3}	Supporting electrolyte	pK_a
0.4	LiOD–LiNO$_3$	13.55
	NaOD–NaNO$_3$	13.25
	KOD–KNO$_3$	13.55
1.0	LiOD–LiNO$_3$	13.45
	NaOD–NaNO$_3$	13.05
	KOD–KNO$_3$	13.30

ethanol to the electrolyte solution. To obtain a reliable ^{13}C signal in the strongly alkaline solutions, *i.e.* pH ≥ 13.5, a greater number of scans was necessary due to the longer relaxation times of the methanediol anion caused by a stronger solvation of the nuclei and the increased viscosity of the solution. However, the chemical shift values were not changed within the measurement error on varying the pulse interval. A shift of the methylene carbon of methanediol to lower fields was observed in all cases with increasing pH of the alkaline solutions. Although the methanediol anion is more strongly solvated in such solutions the deshielding effect of the charged oxygen atom is dominant. The Cannizzaro reaction did not proceed significantly during the period of recording spectra as the probes were analysed by polarography.[17]

The dependences of the ^{13}C chemical shift of methanediol *vs.* pD (Fig. 1) have a form[18,19] typical of titration curves from which pK_a values were determined. We suppose that the conversion of the protonated and the base form of methanediol in eqn. (2) corresponds to a linear scale *vs.* the chemical shift value at least in the range of pH below 13.5, as has analogously been found for carboxylic acids and other small molecules.[20] Thus the pK_a values were taken as the inflection point of the dependence of δ *vs.* pD.

The results obtained show a trend of decrease in pK_a values with increase in ionic strength of the solution (Table 1). The pK_a values of methanediol deprotonation were found to be in the range from 13.05 to 13.55 in CH_2O–D_2O solution depending on the ionic strength and the cation of the supporting electrolyte. This decrease in pK_a values is consistent with the known trend of the influence of ionic strength on the reaction rate constant, *i.e.* the ionic strength does not influence the rate constant of reaction between non-charged species [direct reaction (2)] and increases the rate of reaction involving two species with opposite charge [reverse reaction (2)].[21,22]

When comparing numerical pK_a values at the ionic strengths 0.4 and 1.0 mol dm^{-3} respectively it is seen that the smallest difference is observed in the case of LiOD–LiNO$_3$ as supporting electrolyte and the difference rises in the sequence of alkali-metal ions $Li^+ < Na^+ < K^+$. This can be related to different changes in the activity coefficients of $LiNO_3$, $NaNO_3$ and KNO_3 with increase in concentration, *e.g.* with increase in molal concentration from 0.5 to 1.0 mol kg^{-1} in the case of $LiNO_3$ the activity coefficient changes insignificantly (rises 0.018), and considerably decreases in $NaNO_3$ solution (0.070) and, especially, in KNO_3 solution (0.103).[23]

Experimental

The ^{13}C NMR spectra were recorded on a Tesla BS 587A spectrometer operating at 20 MHz with intervals of 2, 5 and 10 s between the pulses, the probe temperature being 25 ± 1 °C. D_2O with deuterium content 99.8% was used as a solvent and ethanol as internal standard. The chemical shifts were measured relative to the methylene and methyl carbon lines of ethanol with an accuracy of 0.1 ppm. The solutions for spectral measurements were prepared by dissolving known amounts of paraformaldehyde (trioxymethylene) in solutions containing deuteriated alkali-metal hydroxides and nitrates and were allowed to equilibrate for several minutes before recording the spectra. The ionic strength of solutions was kept constant at 0.4 or 1.0 mol dm^{-3}.

The pD of solutions was measured using an EV-74 pH-meter (Belarus). The glass electrode was kept in 0.1 mol dm^{-3} DCl solution before the measurements. The calibration was carried out by taking into account known values of the NaOD activity coefficients in D_2O and the ionic product of D_2O, equal to 14.96.[2]

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References

1 P. Greenzaid, Z. Luz and D. Samuel, *J. Am. Chem. Soc.*, 1967, **89**, 749.
2 A. Calusaru, L. Crisan and J. Kuta, *J. Electroanal. Chem. Interfacial Electrochem.*, 1973, **46**, 51.
3 P. Valenta, *Collect. Czech. Chem. Commun.*, 1960, **25**, 853.
4 J. F. Walker, *Formaldehyde*, Reinhold Publ. Corp., New York, 1964.
5 R. S. Buck and L. R. Griffith, *J. Electrochem. Soc.*, 1962, **109**, 1005.
6 J. E. A. M. van den Meerakker, *J. Appl. Electrochem.*, 1981, **11**, 395.
7 R. Schumacher, J. J. Pesek and O. R. Melroy, *J. Phys. Chem.*, 1985, **89**, 4338.
8 Z. Jusys, *J. Electroanal. Chem. Interfacial Electrochem.*, 1994, **375**, 257.
9 Z. Jusys and A. Vaškelis, *Electrochim. Acta*, 1997, **42**, 449.
10 A. Vaškelis, E. Norkus, R. Juškėnas, E. Matulionis and G. Stalnionis, *Galvanotechnik*, 1995, **86**, 2114.
11 E. Norkus, A. Vaškelis, E. Butkus and Pauliukaitė, *J. Chem. Res.*, 1997, (*S*) 126, (*M*) 0842.
12 D. Barnes and P. Zuman, *J. Electroanal. Chem., Interfacial Electrochem.*, 1973, **46**, 323.
13 R. P. Bell and D. P. Onwood, *Trans. Faraday Soc.*, 1962, **58**, 1557.
14 K. Vesely and R. Brdicka, *Collect. Czech. Chem. Commun.*, 1947, **12**, 313.
15 M. Hellin, J. Delmau and F. Coussemant, *Bull. Soc. Chim. Fr.*, 1967, 3355.
16 I. Ya. Slonim, A. G. Gruznov, T. F. Oreshnikova, V. N. Klyuchnikov, L. M. Romanov and R. Z. Pavlikov, *Vysokomol. Soed.*, 1987, **29**, 282.
17 E. Norkus, Pauliukaitė and A. Vaškelis, *Ber. Bunsenges. Phys. Chem.*, submitted.
18 G. de Vit, A. P. G. Kiebom and H. van Bekkum, *Tetrahedron Lett.*, 1975, 3943.
19 D. L. Holmes and D. A. Lightner, *Tetrahedron*, 1995, **51**, 1607.
20 D. Farcasiu and A. Ghenciu, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1996, **29**, 129.
21 P. C. Jordan, *Chemical Kinetics and Transport*, Plenum Press, New York, 1980.
22 K. A. Connors, *Chemical Kinetics. The Study of Reaction Rates in Solution*, VCH, New York, 1990.
23 D. Dobos, *Electrochemical Data*, Akademiai Kiado, Budapest, 1978.