

# pH Values of the standard tetraborate buffer solution in 50% methanol

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The EMF values of a cell without transference were potentiometrically measured with a hydrogen electrode and silver/silver chloride reference electrode of the standard tetraborate buffer solution in 50% methanol (by weight) at 15, 25, and 35°C. The measured EMF values were used for calculating the conventional values  $p a_{\text{H}}^* = -\log m_{\text{H}} \gamma_{\text{H}}^*$  of the tetraborate buffer solutions in 50% methanol. These values have been recommended for calibration of pH-meter.

Были осуществлены потенциметрические измерения значений ЭДС ячейки без перевода, с водородным электродом и хлоросеребряным электродом сравнения, стандартного буферного раствора в 50%-ном метаноле (весовые %) при 15, 25 и 35°C. По измеренным значениям ЭДС были рассчитаны условные значения  $p a_{\text{H}}^* = -\log m_{\text{H}} \gamma_{\text{H}}^*$  тетраборатных буферных растворов в 50%-ном метаноле, которые рекомендуются для калибровки pH-метра.

New pieces of knowledge about the existence and formation of acidity scales in nonaqueous and mixed solvents have not been propagated enough as yet and therefore they are not applied in practice.

The working pH\* scale which necessitates to know the pH\* (S) values of the primary standards is used for practical acidity measurements of unknown samples in nonaqueous solvent. The asterisk denotes a standard state different from the limiting dilute aqueous solution.

The pH\* values of the primary standards in a solvent may be determined by the method which is known from the defining measurements of the pH values of standards in water [1, 2].

The pH\* values of oxalate [3], succinate [3], acetate [4], and phosphate [4] buffer solutions in 50% methanol were thus obtained and recommended for calibration of pH-meters. Furthermore, the measurements were carried out with the

tris(hydroxymethyl)aminomethane—tris(hydroxymethyl)aminomethane · HCl [5] and 4-aminopyridine—4-aminopyridine · HCl [6] buffer solutions for the purpose of definition. However, these solutions are not suited for calibration of a pH-meter owing to a high value of the residual diffusion potential.

The aim of this study is to obtain the defining  $\text{pH}^*(S)$  values of the tetraborate buffer solution in 50% methanol.

## Experimental

### *Purification of solvent*

Methanol was twice distilled and dried with molecular sieve. The minute amounts of water were estimated by the method according to K. Fischer. The content of water varied within the range 0.008—0.024% (by weight).

### *Purification of chemicals*

Disodium tetraborate was twice crystallized from aqueous solution and dried in desiccator over NaBr [7].

Sodium chloride was purified with gaseous chlorine, precipitated with gaseous hydrogen chloride [7].

### *Measuring device*

The measurements were performed in a vessel of the U form. Two hydrogen electrodes were put in one part of the vessel while three silver/silver chloride reference electrodes were put in another part. Hydrogen moisted with the solution measured was introduced through a capillary and fritted glass into that part of the vessel where the hydrogen electrodes were placed. Hydrogen was produced in a hydrogen generator General Electric. In order to reduce mechanical failures, all combinations of the measured cells which could be obtained in the vessel were made by means of a multiple-pole switch. A thermostat U 10 was used for thermostating. The potential was measured with an integrating digital voltmeter MT 100 (Metra, Blansko).

The solutions were prepared by weighing on an analytical balance (Sartorius 200 g) accurate to  $\pm 0.05$  mg.

The silver/silver chloride electrode was prepared by the thermoelectric method [8] which is based on thermal formation of a silver layer on Pt spiral and electrolytic oxidation of Ag to AgCl in a solution of hydrochloric acid.

The hydrogen electrode was prepared by platinum plating of a platinum electrode (lasting 5—10 min) in a 2% solution of  $\text{H}_2\text{PtCl}_6$  with the current density of 10—20  $\text{mA cm}^{-2}$ .

## Results and discussion

The measurements of the EMF values of the cell Pt, H<sub>2</sub> | buffer solution Y<sub>i</sub> in 50% CH<sub>3</sub>OH | AgCl,Ag were carried out in the vessel described in Experimental. The values obtained were used for calculating the values of  $p_{a_{H^+}}\gamma_{Cl^-}^*$  according to the following equation

$$p_{a_{H^+}}\gamma_{Cl^-}^* = \frac{(E - {}_sE_{Ag/AgCl}^0)E}{2.303 RT} + \log m_{Cl^-} \quad (1)$$

where  $m$  is concentration of the Cl<sup>-</sup> ions in mol kg<sup>-1</sup> and  ${}_sE_{Ag/AgCl}^0$  is the standard potential of the silver/silver chloride electrode in 50% methanol the values of which are given in Table 1.

Table 1

Pressure of saturated vapour of 50% methanol and the values of standard potential of the silver/silver chloride electrode in 50% methanol at different temperatures

Quantity symbol	<i>t</i> /°C		
	15	25	35
$p_{SH}/\text{kPa}$	5.253	9.572	15.598
${}_sE_{Ag/AgCl}^0/\text{V}$	0.19826	0.19058	0.18271

The composition of the solutions measured Y<sub>i</sub> is described in Tables 2 and 6.

The measured EMF values used for calculating  $E$  were corrected on the basis of the following equation

$$E = \text{EMF} + 2.303 \frac{RT}{F} \log \sqrt{\frac{101.325}{p_{H_2}}} \quad (2)$$

where  $p_{H_2}^0$  is 101.325 kPa, *i.e.* the hydrogen pressure of the standard hydrogen electrode,  $p_{H_2}$  is the real hydrogen pressure during measurement calculated from the equation

$$p_{H_2} = p_B - p_{SH} + 3.92 h \quad (3)$$

$p_B$  is barometric pressure,  $p_{SH}$  is the pressure of saturated vapour of 50% methanol at the temperature of measurement, and  $h$  is the dipping depth of the inlet tube in mm. The last term in eqn (3) was very small and could be omitted in calculations.

The pressure of saturated vapour of 50% methanol  $p_{SH}$  and the standard potential of the silver/silver chloride reference electrode were taken from Ref. [9] and the values presented in Table 1 were used for particular temperatures.

The values of  $p_{a_{H^+}}\gamma_{Cl^-}^*$  obtained with the acetate and tetraborate buffer solutions of different total concentrations of the buffer mixture are given for three different temperatures in Table 2.

Table 2

Values  $p_{a_{H^+}}\gamma_{Cl^-}^*$  for the tetraborate and acetate buffer solutions in 50% methanol

Buffer solution mol kg <sup>-1</sup>	<i>I</i> /mol kg <sup>-1</sup>	$p_{a_{H^+}}\gamma_{Cl^-}^*$		
		15°C	25°C	35°C
0.005 Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> + 0.010 NaCl	0.02	9.30	9.39	9.42
0.010 Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> + 0.020 NaCl	0.04	9.35	9.42	9.46
0.015 Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> + 0.030 NaCl	0.06	9.39	9.45	9.49
0.020 Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> + 0.040 NaCl	0.08	9.45	9.50	9.54
0.025 Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> + 0.050 NaCl	0.10	9.43	9.52	9.52
0.020 CH <sub>3</sub> COOH + + 0.020 CH <sub>3</sub> COONa + 0.020 NaCl	0.04	5.69	5.68	5.68
0.030 CH <sub>3</sub> COOH + + 0.030 CH <sub>3</sub> COONa + 0.030 NaCl	0.06	5.67 <sup>a</sup>	5.66 <sup>a</sup>	5.67 <sup>a</sup>
0.040 CH <sub>3</sub> COOH + + 0.040 CH <sub>3</sub> COONa + 0.040 NaCl	0.08	5.66	5.68	5.67
0.050 CH <sub>3</sub> COOH + + 0.050 CH <sub>3</sub> COONa + 0.050 NaCl	0.10	5.67 <sup>a</sup>	5.66 <sup>a</sup>	5.67 <sup>a</sup>
		5.63	5.64	5.65
		5.67 <sup>a</sup>	5.66 <sup>a</sup>	5.67 <sup>a</sup>
		5.67 <sup>a</sup>	5.64	5.65
		5.67 <sup>a</sup>	5.66 <sup>a</sup>	5.67 <sup>a</sup>

a) Data from literature [6].

In order to confirm the correctness of the values obtained by us, we measured the acetate buffer mixtures which had been measured earlier by *Bates* and coworkers [4]. Our values of  $p_{a_{H^+}}\gamma_{Cl^-}^*$  are compared in Table 2 with the values of the acetate buffer solutions found in literature. Because of good agreement of our results with reported values, we may assume that the values of  $p_{a_{H^+}}\gamma_{Cl^-}^*$  obtained for the tetraborate mixtures are correct and may serve as a basis for calculating the  $p_{a_{H^+}}$  values of the conventional scale in 50% methanol. In order to find out whether a dependence of the  $p_{a_{H^+}}\gamma_{Cl^-}^*$  values on concentration of the chloride ions exists in the buffer solutions investigated, we took one constant concentration for each buffer mixture and varied only the concentration of the chloride ions. The EMF measurements were carried out in a cell without transference at 25°C. Like in the preceding case, the measured EMF values were corrected for real hydrogen pressure and used for calculating  $p_{a_{H^+}}\gamma_{Cl^-}^*$ . The values obtained with the acetate and tetraborate buffer solutions are given in Tables 3 and 4.

The dependence of  $p_{a_{H^+}}\gamma_{Cl^-}^*$  on concentration of the chloride ions in both solutions was processed by linear regression. The results found for the acetate and tetraborate buffer solutions are presented in Table 5.

Table 3

Dependence of  $p a_{H^+} \gamma_{Cl^-}^*$  on concentration of the  $Cl^-$  ions ( $x$ ) in the acetate buffer solution at 25°C  
 Buffer solution: 0.05 mol kg<sup>-1</sup> CH<sub>3</sub>COOH + 0.05 mol kg<sup>-1</sup> CH<sub>3</sub>COONa +  $x$  mol kg<sup>-1</sup> in 50% methanol

$x/\text{mol kg}^{-1}$	$I/\text{mol kg}^{-1}$	$p a_{H^+} \gamma_{Cl^-}^*$
0.03	0.08	5.61
0.04	0.09	5.59
0.05	0.10	5.59
0.10	0.15	5.61
0.15	0.20	5.62

Table 4

Dependence of  $p a_{H^+} \gamma_{Cl^-}^*$  on concentration of the  $Cl^-$  ions ( $x$ ) in the tetraborate buffer solution at 25°C  
 Buffer solution: 0.01 mol kg<sup>-1</sup> Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> +  $x$  mol kg<sup>-1</sup> NaCl in 50% methanol

$x/\text{mol kg}^{-1}$	$I/\text{mol kg}^{-1}$	$p a_{H^+} \gamma_{Cl^-}^*$
0.005	0.025	9.39
0.010	0.030	9.39
0.020	0.040	9.42
0.025	0.045	9.42
0.030	0.050	9.42

Table 5

Linear regression for the acetate and tetraborate buffer solutions and their  $p(a_{H^+}^*)^0$  values

Buffer solution mol kg <sup>-1</sup>	$p(a_{H^+} \gamma_{Cl^-}^*)^0$	Slope	Correlation coefficient	$p(a_{H^+}^*)^0$
0.05 CH <sub>3</sub> COOH + 0.05 CH <sub>3</sub> COONa	5.604	0.1897	0.7112	5.47
0.01 Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	9.381	1.465	0.924	9.25

On the basis of the results of linear regression we did not find an unambiguous dependence of the  $p a_{H^+} \gamma_{Cl^-}^*$  values on concentration of the chloride ions in the acetate solution (Table 5). Therefore we calculated the  $p(a_{H^+} \gamma_{Cl^-}^*)^0$  value as the average value of  $p a_{H^+} \gamma_{Cl^-}^*$  from the data given in Table 3. Other authors who performed the defining measurements of the pH\* (S) standards for water—methanol [3] and water—ethanol [10] mixtures also came to similar conclusions.

The value of  $p(a_{H^+} \gamma_{Cl^-}^*)^0$  found by linear regression for the tetraborate buffer solution is given in Table 5. The  $p a_{H^+}^*$  values of the acetate and tetraborate buffer

solutions without any addition of alkaline chloride were calculated from the  $p(a_{\text{H}^+}\gamma_{\text{Cl}^-}^*)^0$  values (Table 5). Both buffer mixtures are to be recommended for calibrating glass electrode in the  $\text{pH}^*$  measurements in 50% methanol.

The  $\text{pa}_{\text{H}^+}^*$  values of other buffer solutions (with addition of alkaline halogenide) were calculated from the measured  $\text{pa}_{\text{H}^+}\gamma_{\text{Cl}^-}^*$  values by using the convention [4] that the value  $\hat{a} = 4.56 \times 10^{-10}$  m was used as  $\hat{a}$  parameter for the chloride ion. The relative permittivities and the values of constants  $A$  and  $B$  in the Debye—Hückel relationship for 50% methanol at different temperatures were taken from paper [9].

Table 6

$\text{pa}_{\text{H}^+}^*$  Values of the buffer solutions in 50% methanol

Buffer: solution mol kg <sup>-1</sup>	$I/\text{mol kg}^{-1}$	$\text{pa}_{\text{H}^+}^*$		
		15°C	25°C	35°C
0.005 Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> + 0.010 NaCl	0.02	9.21	9.30	9.32
0.010 Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> + 0.020 NaCl	0.04	9.23	9.30	9.33
0.015 Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> + 0.030 NaCl	0.06	9.25	9.31	9.35
0.020 Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> + 0.040 NaCl	0.08	9.30	9.34	9.38
0.025 Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> + 0.050 NaCl	0.10	9.27	9.35	9.35
0.020 CH <sub>3</sub> COOH + + 0.020 CH <sub>3</sub> COONa + 0.020 NaCl	0.04	5.58	5.55	5.55
0.030 CH <sub>3</sub> COOH + + 0.030 CH <sub>3</sub> COONa + 0.030 NaCl	0.06	5.53 <sup>a</sup>	5.54 <sup>a</sup>	5.54 <sup>a</sup>
0.040 CH <sub>3</sub> COOH + + 0.040 CH <sub>3</sub> COONa + 0.040 NaCl	0.08	5.53 <sup>a</sup>	5.52 <sup>a</sup>	5.52 <sup>a</sup>
0.050 CH <sub>3</sub> COOH + + 0.050 CH <sub>3</sub> COONa + 0.050 NaCl	0.10	5.48	5.49	5.49
		5.52 <sup>a</sup>	5.50 <sup>a</sup>	5.51 <sup>a</sup>
		5.50	5.48	5.48
		5.50 <sup>a</sup>	5.49 <sup>a</sup>	5.50 <sup>a</sup>

a) Data from literature [6].

Table 6 contains the recommended  $\text{pa}_{\text{H}^+}^*$  values for the acetate buffer solutions with an addition of NaCl based on this work and literature [4] as well as the recommended  $\text{pa}_{\text{H}^+}^*$  values for the tetraborate buffer solutions with an addition of NaCl obtained in this study.

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