

pH* Values of the etalon acetate and oxalate buffer solution in the acetone—water solution with mass fraction $w(\text{acetone}) = 50\%$

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The EMF values of the cell without liquid junction were measured potentiometrically with palladium-plated hydrogen electrode and silver/silver chloride electrode in the standard acetate and oxalate buffer solution dissolved in the acetone—water solvent with mass fraction $w(\text{acetone}) = 50\%$. The obtained EMF values were used for calculating the conventional $p_{a\ddot{H}}$ values of the buffer solutions which were used for calibrating the pH-meter. Further buffer solutions in the above mixed solvent were prepared for different types of potentiometric cells with liquid junction in the working pH* scale. The pH* values thus obtained were compared with the pH* values obtained in the concentration scale. The capacities of selected acetate and oxalate buffer solutions, their dilution factors, and correction factor for the acetone—water solvent with $w(\text{acetone}) = 50\%$ were determined.

Проведены потенциметрические измерения величин ЭДС в гальваническом элементе без переноса с водородным палладированным и хлорсеребряным электродами стандартных ацетатного и оксалатного буферных растворов в растворителе ацетон—вода с долей по массе $w(\text{ацетон}) = 50\%$. На основании найденных величин ЭДС были рассчитаны величины $p_{a\ddot{H}}$ упомянутых буферных растворов, использованные для калибровки pH-метра. Были проведены измерения для других буферных растворов в упомянутом смешанном растворителе в потенциметрических элементах с переносом различных типов в рабочем диапазоне pH*. Таким образом полученные значения pH* были сравнены с величинами pH*, полученными исходя из концентрационной шкалы. Были определены емкости выбранных ацетатных и оксалатных буферных растворов, их фактор разбавления и поправочный фактор для растворителя ацетон—вода $w(\text{ацетон}) = 50\%$.

The pH* values of primary standards in the acetone—water solvent may be determined analogously as in the methanol—water [1] or ethanol—water solvent [2]. Sufficient attention has not yet been paid to the formation of acidity scales in the medium of pure acetone or its mixtures with water. *Lebedeva* [3] proposed some standards for the mixed acetone—water solvent with mass fraction

$w(\text{acetone}) = 30\%$, 50% , and 70% from which the etalon solution may be prepared for defining the conventional and working pH^* scale. The values of $\text{p}a_{\text{H}^+}^{\ddagger}$ and $\text{p}(a_{\text{H}^+} \cdot \gamma_{\text{Cl}^-}^{\ddagger})$ obtained for the acetone—water solvent with mass fraction $w(\text{acetone}) = 70\%$ and 80% containing potassium hydrogen phthalate, bipotassium tetraoxalate, and salicylate or benzoate buffer solution are presented in paper [4].

The aim of this study was to obtain the definition values $\text{p}a_{\text{H}^+}^{\ddagger} = \text{pH}^*(\text{S})$ for the acetate and oxalate buffer solution in the acetone—water solvent with $w(\text{acetone}) = 50\%$ and to estimate the possibilities of using them as etalon solutions for defining the pH^* scale in this solvent. Another aim was to compare different methods of acidity measurement in this mixed solvent and to determine the value of correction factor δ necessary for transforming the pH values obtained in the aqueous working scale to the pH^* values. As for the etalon buffer solutions, we wanted to determine not only the pH^* values, but also buffer capacities and dilution factor.

Experimental

Purification of solvents and chemicals

Acetone, anal. grade, was dehydrated with activated molecular sieve Potasit 3A (100 g of molecular sieve per 2 dm^3 of acetone). After standing for 24 h, acetone was distilled through a glass column of 0.6 m length filled with glass rings. The content of water was determined by gas chromatography ($w(\text{H}_2\text{O}) = 0.01\text{—}0.03\%$). The density and index of refraction were compared with the tabulated values.

Ammonium hydrogen oxalate was recrystallized from the mixed ethanol—water solvent ($\varphi(\text{ethanol}) = 50\%$).

Other chemicals were purified according to literature: acetic acid [5], sodium acetate [6], NaCl, HCl, and oxalic acid [7] (p. 24, 37, and 40).

Measuring equipments

Electrodes

Silver/silver chloride electrode prepared by thermoelectrolytic procedure [8].

Hydrogen electrode with Palladium Black [9].

Calomel electrode K 401 (Radiometer).

Glass electrode G 202 B (Radiometer).

The definition $\text{p}a_{\text{H}^+}^{\ddagger}$ measurements of buffer solutions in the acetone—water solvent ($w(\text{acetone}) = 50\%$) were performed according to [1]. The pH^* values of buffer solutions in the cells with liquid junction containing the above mixed solvent were measured as described earlier [2, 10].

Apparatuses

The potentiometric measurements with hydrogen electrode were carried out by using a digital voltmeter TR 1652-2 (Hungary). A digital pH-meter PHM 64 (Radiometer) was used for measurements with glass electrode. Hydrogen was developed electrolytically in a hydrogen generator (General Electric, USA). A thermostat U 10 (GDR) was applied to thermostating. Barometric pressure was measured with a precision station barometer (GDR) accurate to ± 13.3 Pa.

Measuring cells

Cell A: Pd(H₂) | solution S in the acetone—water solvent ($w(\text{acetone}) = 50\%$) | AgCl; Ag.

Cell B: Glass electrode | solution S or X || saturated KCl in the acetone—water solvent ($w(\text{acetone}) = 50\%$) | AgCl; Ag.

Cell C: Glass electrode | solution S or X || saturated KCl in H₂O | Hg₂Cl₂; Hg.

The measured definition values of EMF of cell A were used for calculating the $p a_{\text{H}^+}^{\#}$ values by the method described in paper [1]. The pH* values in the working and concentration scale were calculated from the measured values of EMF of cells B and C by the method presented in paper [2].

Table 1

Values of E_{cor} and $p(a_{\text{H}^+} \cdot \gamma_{\text{Cl}^-}^*)$ of the acetate and oxalate buffer solutions in the acetone—water solvent with $w(\text{acetone}) = 50\%$ at 25 °C

Buffer solution	$\frac{\sum_i m_i}{\text{mol kg}^{-1}}$	$\frac{I}{\text{mol kg}^{-1}}$	$\frac{E_{\text{cor}}}{\text{mV}}$	s_{R}	$p(a_{\text{H}^+} \cdot \gamma_{\text{Cl}^-}^*)$
0.02HAc + 0.02NaAc + 0.02NaCl		0.04	633.55	0.272	6.24
0.02HAc + 0.02NaAc + 0.05NaCl		0.05	618.51	0.067	6.16
0.02HAc + 0.02NaAc + 0.04NaCl		0.06	620.71	0.096	6.23
0.02HAc + 0.02NaAc + 0.06NaCl		0.08	602.90	0.152	6.20
0.02HAc + 0.02NaAc + 0.08NaCl		0.10	599.91	0.131	6.28
0.01HOx + 0.01NH ₄ HOx + 0.01NaCl		0.02	470.20	0.072	3.18
0.01HOx + 0.01NH ₄ HOx + 0.02NaCl		0.03	452.02	0.061	3.17
0.01HOx + 0.01NH ₄ HOx + 0.03NaCl		0.04	441.26	0.080	3.16
0.01HOx + 0.01NH ₄ HOx + 0.05NaCl		0.06	428.62	0.104	3.17
0.01HOx + 0.01NH ₄ HOx + 0.07NaCl		0.08	419.81	0.078	3.18
0.01HOx + 0.01NH ₄ HOx + 0.09NaCl		0.10	412.87	0.081	3.16

HAc — acetic acid, NaAc — sodium acetate, HOx — oxalic acid, NH₄HOx — ammonium hydrogen oxalate.

Results and discussion

The composition of the measured definition buffer solutions in the mixed acetone—water solvent ($w(\text{acetone}) = 50\%$) is given in Table 1. The measured

and corrected values of EMF which are the average of six measurements in independent cells and were used for calculating the values $p(a_{\text{H}^+} \cdot \gamma_{\text{Cl}^-}^*)$ are also presented in Table 1. The value of s_R for the corrected values of EMF was calculated from spreading. The dependence of the values of $p(a_{\text{H}^+} \cdot \gamma_{\text{Cl}^-}^*)$ on molality of the chloride ions was processed by linear regression by using the method of least squares. The numerical value of $p(a_{\text{H}^+} \cdot \gamma_{\text{Cl}^-}^*)^0$ was obtained as section on the y axis for zero relative molality of the chloride ions by linear regression of the equation

$$p(a_{\text{H}^+} \cdot \gamma_{\text{Cl}^-}^*) = f(m_{\text{Cl}^-})$$

The values of standard potential of the reference electrode and other constants of the mixed solvent necessary for calculation of the values of $p(a_{\text{H}^+} \cdot \gamma_{\text{Cl}^-}^*)$ from the values of EMF are given in paper [9]. The standard potential of the reference electrode in the above solvent is equal to $E^\circ = 163.77$ mV.

The value of $pa_{\text{H}^+}^*$ of the acetate buffer solution (solution II) in the mixed acetone—water solvent ($w(\text{acetone}) = 50\%$) at 25°C is 5.97 and the value appertaining to the oxalate buffer solution (solution I) in this mixed solvent is 2.72. These buffer solutions were employed as etalon solutions for measuring pH^* of other buffer solutions in the working scale by the use of cells B and C.

One acetate and one oxalate solution with an admixture of NaCl for adjusting the ionic strength to the value $I = 0.10$ mol kg^{-1} (solutions III and IV) were used as etalon solutions of the first order in further measurements in the working pH^* scale.

In order to characterize fully etalon buffer solutions I and II, their buffer capacities and dilution factors were measured by the method described in publication [11]. The results are given in Table 2.

Table 2

Buffer capacities and dilution factors of the acetate and oxalate solutions in the acetone—water solvent with $w(\text{acetone}) = 50\%$ at 25°C

Buffer solution	$\frac{\sum m_i}{\text{mol kg}^{-1}}$	$\frac{\beta_{\text{HCl}}}{\text{mol kg}^{-1}}$	$\frac{\beta_{\text{NaOH}}}{\text{mol kg}^{-1}}$	$\Delta\text{pH}_{f/2}^*$
0.02 $\text{CH}_3\text{COOH} + 0.02\text{CH}_3\text{COONa}$ (II)		0.018	0.028	0.03
0.01 $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} + 0.01\text{NH}_4\text{HCO}$ (I)		0.020	0.026	0.03

It results from comparison of the characteristic parameters β_{HCl} , β_{NaOH} , and $\Delta\text{pH}_{f/2}$ found in the mixed acetone—water solvent ($w(\text{acetone}) = 50\%$) for etalon

Table 3

Confrontation of different methods of pH* measurement in the acetone–water solvent with $w(\text{acetone}) = 50\%$ at $25\text{ }^\circ\text{C}$

Buffer solution $\frac{\sum m_i}{\text{mol kg}^{-1}}$	$\frac{I}{\text{mol kg}^{-1}}$	Working pH* scale		Working pH* scale	Concentration scale	Definition values $p_a^{\#}$
		Nonaqueous standards		Aqueous standard	HCl standards	
		pH* (B)	pH* (C)	pH* = "pH" – δ	pH* (C)	
0.01HOx + 0.01NH ₄ HOx (I)	0.01			2.71 ± 0.02	2.70 ± 0.03	2.72
0.01HOx + 0.01NH ₄ HOx + 0.09NaCl (III)	0.10	2.72 ± 0.01	2.70 ± 0.02	2.72 ± 0.02	2.70 ± 0.03	2.71
0.02HAc + 0.02NaAc (II)	0.02	5.97 ± 0.02	5.99 ± 0.02	5.98 ± 0.02	5.97 ± 0.04	5.97
0.05HAc + 0.05NaAc + 0.05NaCl	0.10	6.03 ± 0.01	6.03 ± 0.02	6.03 ± 0.02	6.04 ± 0.02	6.03
0.02HAc + 0.02NaAc + 0.08NaCl (IV)	0.10	6.07 ± 0.01	6.08 ± 0.02	6.07 ± 0.02	6.07 ± 0.03	6.07
0.02NaHSucc + 0.08NaCl	0.10	6.29 ± 0.02	6.30 ± 0.01	6.28 ± 0.04	6.30 ± 0.03	
0.05NaHSucc + 0.05NaCl	0.10	6.26 ± 0.02	6.27 ± 0.01	6.27 ± 0.03	6.29 ± 0.04	
0.02NaHSucc	0.02	6.43 ± 0.01	6.42 ± 0.01	6.42 ± 0.01	6.45 ± 0.03	
0.01TRIS + 0.01TRIS · HCl	0.01	7.84 ± 0.01	7.83 ± 0.02	7.83 ± 0.02	7.83 ± 0.03	
0.01TRIS + 0.01TRIS · HCl + 0.09NaCl	0.10	7.90 ± 0.02	7.91 ± 0.01	7.90 ± 0.01	7.89 ± 0.02	
0.03TRIS + 0.03TRIS · HCl	0.03	7.94 ± 0.02	7.95 ± 0.02	7.91 ± 0.03	7.94 ± 0.03	
0.03TRIS + 0.03TRIS · HCl + 0.05NaCl	0.08	8.04 ± 0.02	8.05 ± 0.02	8.05 ± 0.03	8.03 ± 0.02	

HOx — oxalic acid, HAc — acetic acid, NH₄HOx — ammonium hydrogen oxalate, NaAc — sodium acetate, NaHSucc — sodium hydrogen succinate, TRIS — tris(hydroxymethyl)aminomethane.

solutions I and II with the values found for similar etalon solutions in water or methanol—water mixtures [12] that our experimental values of β and $\Delta\text{pH}_{1/2}$ are of equal decimal order as values found in the mentioned solvents. On the basis of this fact, we may state that the behaviour of buffer solutions in the acetone—water solvent ($w(\text{acetone}) = 50\%$) does not substantially differ from their behaviour in water.

Table 3 summarizes the results obtained by measuring the pH^* values of standard buffer solutions I, II, III, and IV and other buffer solutions (Succ and TRIS solution) in cells with liquid junction (cells B and C).

Several methods of calibration of the measuring cell were used in these measurements like in study [10]. For the first kind of calibration some nonaqueous standards were used and the measurements were carried out in both types of cells (B, C). For the second kind of calibration the aqueous phosphate standard buffer solution S 1326 (Radiometer) with $\text{pH} = 7.00 \pm 0.01$ at 25°C was used. The apparent values “ $\text{pH}(\text{X})$ ” were transformed to $\text{pH}^*(\text{X})$ by means of the correction factor δ as described in paper [10].

Our value of δ for the mixed acetone—water solvent ($w(\text{acetone}) = 50\%$) was experimentally determined by the procedure described in paper [13]. This value ($\delta = -0.12$) is in good agreement with analogous data recorded in literature for mixed acetone—water solvents with other mass fractions (Table 4).

Table 4

Values of the correction factor δ — data taken from Ref. [11] for acetone—water mixtures at 25°C

$w(\text{acetone})/\%$	δ
17.8	-0.04
36.4	-0.06
45.9	-0.09
50.0	-0.12*
55.8	-0.15
65.9	-0.29
76.5	-0.57
87.9	-1.33
93.8	-2.33

* Determined by us.

In the third kind of calibration the pH^* values were obtained from the “concentration” scale and the experimental pmH values were transformed to the pH^* values by means of the activity coefficient $\gamma_{\text{H}^+}^*$ appertaining to the mixed

acetone—water solvent ($w(\text{acetone}) = 50\%$). For the measurements in the “concentration” scale this scale was calibrated by means of solutions of HCl in the acetone—water mixture ($w(\text{acetone}) = 50\%$) with graduated molality and constant ionic strength $I = 0.10 \text{ mol kg}^{-1}$. For this reason, besides etalon solutions I and II we also prepared etalon solutions III and IV which had similar composition as I and II but constant ionic strength $I = 0.10 \text{ mol kg}^{-1}$. The ionic strength was adjusted by adding NaCl to the components of buffer solution.

By comparing three kinds of formation of acidity scales in the mixed acetone—water solvent with mass fraction $w(\text{acetone}) = 50\%$, it has been disclosed that, like in the mixed methanol—water ($w(\text{CH}_3\text{OH}) = 50\%$) [12] and ethanol—water solvent ($w(\text{C}_2\text{H}_5\text{OH}) = 50\%$) [2], the measurements of acidity in the working pH^* scale by the use of aqueous etalon solutions and correction factor δ are less precise and correct and, as a matter of fact, are only rough approximation to the correct value. The concentration scale also gives less correct and precise results, the precision of which is approximately equal to the precision of the pH^* measurements involving the correction factor δ (wider intervals of reliability). The drawback of the concentration scale consists in the necessity to work at constant ionic strength not only in the course of calibration but also of measurements themselves. If the ionic strength of the measured solutions is substantially different from the ionic strength of the calibration solutions (e.g. solutions I and II), the results are less reproducible or even less correct. These conclusions are valid for solutions with ionic strength $I \leq 0.10 \text{ mol kg}^{-1}$. The measurements in concentration scale are necessary for solutions with higher ionic strength which usually do not need any etalon buffer solutions to be prepared.

At conclusion we may state that the investigated solutions, i.e. solution I ($0.01 \text{ mol kg}^{-1} \text{ HOx} + 0.01 \text{ mol kg}^{-1} \text{ NH}_4\text{HOx}$) and solution II ($0.02 \text{ mol kg}^{-1} \text{ HAc} + 0.02 \text{ mol kg}^{-1} \text{ NaAc}$) may be used as etalon solutions for pH^* measurement in the mixed acetone—water solvent with $w(\text{acetone}) = 50\%$.

A certain drawback of the preparation of solution II consists in the fact that acetic acid is hardly to be kept for long in a defined state as reference material. For this reason, it would be necessary to choose for this pH^* region an etalon solution prepared from better definable reference material (in the form of crystalline solid phase).

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