

Etalon buffer solutions in the mixed ethanol—water solvent

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The cells without liquid junction comprehending hydrogen electrode, silver/silver chloride electrode and electrolyte solutions consisting of the hydrogen phthalate or tetraborate buffer solution in mixed ethanol—water solvents were constructed.

The mass fractions of alcohol in mixed solvents were $w(\text{C}_2\text{H}_5\text{OH}) = 0.3; 0.5; 0.7$.

The values of EMF of these cells measured at 25 °C were used for calculating the conventional $p_{\text{H}}^{\#}$ values of the buffer solutions which were recommended as primary etalon solutions of the first order for reproduction of the $p\text{H}^*$ value.

Furthermore, the cells with liquid junction comprehending glass electrode, silver/silver chloride electrode and electrolytes containing the oxalate, hydrogen succinate, and phosphate buffer solution in mixed ethanol—water solvents were also prepared.

The values of EMF of the cells with liquid junction measured at 25 °C were used for calculating the $p\text{H}^*$ values of the corresponding buffer solutions in respect of the relation valid for the operational scale of $p\text{H}^*$. These buffer solutions were recommended as secondary etalon solutions for reproduction of the $p\text{H}^*$ value. The buffer capacities and dilution values of all etalon solutions were determined.

Были составлены гальванические элементы без переноса, состоящие из водородного и хлорсеребрянного электродов и содержащие гидрофталатный или тетраборный буферные растворы в смешанных растворителях этанол—вода.

Доли по массе этанола в смешанных растворителях были $w(\text{C}_2\text{H}_5\text{OH}) = 0,3; 0,5; 0,7$.

На основании измеренных величин ЭДС этих элементов при 25 °C были рассчитаны величины $p_{\text{H}}^{\#}$ буферных растворов, которые были рекомендованы в качестве первичных эталонных растворов I порядка для воспроизведения величины $p\text{H}^*$.

Были составлены также элементы с переносом со стеклянным и хлорсеребрянным электродами с электролитами, содержащими ок-

салатный, янтарнокислый и фосфатный буферные растворы в смешанных растворителях этанол—вода приведенного состава.

Величины ЭДС, измеренные при 25 °C в элементах с переносом были использованы для расчета значений pH^* соответствующих буферных растворов с помощью соотношения для операционной шкалы pH^* . Эти буферные растворы были рекомендованы в качестве вторичных эталонных растворов для воспроизведения величины pH^* . Была определена также буферная емкость и фактор разбавления для всех эталонных растворов.

The etalon buffer solutions are used for measuring the pH^* value in the mixed ethanol—water solvent like in the mixed methanol—water solvent [1].

The aim of this study has been to obtain the p_{aH}^* values of the hydrogen phthalate and tetraborate buffer solution in the mixed ethanol—water solvents with different mass fractions at 25 °C as well as to estimate the pH^* values of other buffer solutions in these solvents from the working pH^* scale. A full characterization of the etalon buffer solutions required to ascertain their buffer capacity and dilution value.

Experimental

Chemicals

Ethanol for UV spectroscopy was used for the preparation of mixed solvent without further purification. The content of water in ethanol was determined by the method according to K. Fischer. The content of acidic and basic impurities could not be detected by current volumetric methods. Ethanol was diluted with redistilled water.

Other chemicals used were anal. grade reagents. They were purified by the procedures mentioned in paper [2] where the measuring instruments, electrode systems and working procedures are described.

Equal relationships as in paper [1] have been used for calculating the values of p_{aH}^* and pH^* as well as the values of buffer capacity β .

Results and discussion

The primary etalon buffer solutions in the mixed ethanol—water solvents with different mass fractions of ethanol (0.3; 0.5; 0.7) which served as electrolytes for the cells without liquid junction containing an indication hydrogen electrode and reference silver/silver chloride electrode exhibited the composition



and

$$0.010 \text{ mol kg}^{-1} \text{ Na}_2\text{B}_4\text{O}_7 + y \text{ mol kg}^{-1} \text{ NaCl}$$

where $y = 0.002; 0.004; 0.006; 0.008; 0.01$.

The values of $p(a_{\text{H}^+} \cdot \gamma_{\text{Cl}^-}^*)$ of buffer solution in individual solvents were calculated from the measured and corrected values of EMF of these cells. Their dependence on molality of the Cl^- ions was processed by linear regression.

The values of $p(a_{\text{H}^+} \cdot \gamma_{\text{Cl}^-}^*)^\circ$ given in Tables 1 and 2 were obtained as section on the y axis for zero relative molality of the chloride ions according to the linear relationship $p(a_{\text{H}^+} \cdot \gamma_{\text{Cl}^-}^*) = f(m_{\text{Cl}^-})$.

Table 1

Characteristic values of hydrogen phthalate buffer solution (I) in mixed ethanol—water solvents at 25 °C

	$w(\text{C}_2\text{H}_5\text{OH}) = 0.3$	$w(\text{C}_2\text{H}_5\text{OH}) = 0.5$	$w(\text{C}_2\text{H}_5\text{OH}) = 0.7$
$p(a_{\text{H}^+} \cdot \gamma_{\text{Cl}^-}^*)^\circ$	4.919 ± 0.010	5.308 ± 0.010	5.819 ± 0.017
$pa_{\text{H}^+}^\ddagger$	4.83 ± 0.01	5.19 ± 0.01	5.66 ± 0.02
$\Delta p\text{H}_{1/2}^\ddagger$	0.090	0.090	0.020
β	0.020	0.017	0.025

Table 2

Characteristic values of tetraborate buffer solution (II) in mixed ethanol—water solvents at 25 °C

	$w(\text{C}_2\text{H}_5\text{OH}) = 0.3$	$w(\text{C}_2\text{H}_5\text{OH}) = 0.5$
$p(a_{\text{H}^+} \cdot \gamma_{\text{Cl}^-}^*)^\circ$	10.111 ± 0.018	10.647 ± 0.024
$pa_{\text{H}^+}^\ddagger$	10.03 ± 0.02	10.54 ± 0.02
$\Delta p\text{H}_{1/2}^\ddagger$	0.040	0.130
β	0.042	0.013

Then these values gave the $pa_{\text{H}^+}^\ddagger$ values which were also included in Tables 1 and 2. The $pa_{\text{H}^+}^\ddagger$ values thus obtained may be regarded as defined values of the primary etalon buffer solutions which are used for transfer of the pH values in measurements performed in the working scale (cell with liquid junction).

Table 1 contains the characteristic values of the hydrogen phthalate buffer solution (I) in three mixed solvents at 25 °C. The characteristic values of the

tetraborate buffer solution (II) could be measured only in two mixed solvents because the solubility of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ in the mixed solvent with $w(\text{C}_2\text{H}_5\text{OH}) = 0.7$ was very low owing to which we were not able to prepare a solution with sufficiently high molality and buffer capacity as well.

Table 3

pH^* Values of buffer solutions obtained from the working scale for calibration of the measuring cell with primary etalon buffer solutions in mixed ethanol—water solvents at 25 °C

Buffer solution $m / (\text{mol kg}^{-1})$	$w(\text{C}_2\text{H}_5\text{OH}) = 0.3$	$w(\text{C}_2\text{H}_5\text{OH}) = 0.5$	$w(\text{C}_2\text{H}_5\text{OH}) = 0.7$
0.01($\text{H}_2\text{C}_2\text{O}_4 + \text{NH}_4\text{HC}_2\text{O}_4$)	2.39 ± 0.02	2.44 ± 0.01	2.88 ± 0.02
0.05($\text{NaHC}_4\text{H}_4\text{O}_4$)	2.41 ± 0.03	2.46 ± 0.02	6.25 ± 0.01
	5.31 ± 0.02	5.67 ± 0.02	
0.02($\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$)	5.30 ± 0.04	5.67 ± 0.02	
	7.47 ± 0.03	7.66 ± 0.02	
	7.47 ± 0.02	7.67 ± 0.03	

The pH^* values of other buffer solutions obtained from the working scale in the course of calibration of the measuring cell by means of the etalon buffer solutions I and II in the mixed ethanol—water solvents are listed in Table 3. The composition of the selected buffer solutions was consistent with compositions of analogous solutions used earlier [1]. It was as follows

0.01 mol kg^{-1} $\text{H}_2\text{C}_2\text{O}_4 + 0.01$ mol kg^{-1} $\text{NH}_4\text{HC}_2\text{O}_4$ — oxalate buffer solution

0.05 mol kg^{-1} $\text{NaHC}_4\text{H}_4\text{O}_4$ — succinate buffer solution

0.02 mol kg^{-1} $\text{KH}_2\text{PO}_4 + 0.02$ mol kg^{-1} Na_2HPO_4 — phosphate buffer solution

Each column in Table 3 contains two pH^* values for individual buffer solutions (except solution with $w(\text{C}_2\text{H}_5\text{OH}) = 0.7$) with the corresponding interval of reliability. The first value corresponds to the result for calibration of the measuring cell with the etalon buffer solution I while the second value was obtained for calibration of the measuring cell with the etalon buffer solution II. The intervals of reliability of the measured values were processed statistically from 3—5 experimental results by using the range for 95 % probability.

The phosphate buffer solution was also subjected to measurement in the solvent with $w(\text{C}_2\text{H}_5\text{OH}) = 0.7$. Nevertheless, the obtained values are relatively low, which indicates that the pertinent phosphates are not sufficiently soluble in this solvent.

The consistency of the pH^* values obtained on the basis of calibration of the measuring cell with two etalon buffer solutions is very good. The differences between individual pH^* values are in the range 0.01—0.07 pH^* units, which is,

with respect to the mixed medium, in harmony with achievable experimental reproducibility of the results. The difference between the mean pH^* values obtained with two etalon buffer solutions does not exceed 0.02 pH^* units. The buffer solutions the characteristic parameters of which are given in Table 3 may be recommended as secondary etalon buffer solutions for transfer of the pH^* value.

In order to obtain full characterization of the etalon buffer solutions in mixed ethanol—water solvents, we also determined the buffer capacities β and dilution values $\Delta\text{pH}_{1/2}^*$ of these solutions. The obtained experimental results are presented in Tables 1, 2, and 4.

Table 4

Dilution values and buffer capacities of buffer solutions in mixed ethanol—water solvents at 25 °C

Buffer solution <i>m</i> /(mol kg ⁻¹)	$w(\text{C}_2\text{H}_5\text{OH})=0.3$		$w(\text{C}_2\text{H}_5\text{OH})=0.5$		$w(\text{C}_2\text{H}_5\text{OH})=0.7$	
	$\Delta\text{pH}_{1/2}^*$	β	$\Delta\text{pH}_{1/2}^*$	β	$\Delta\text{pH}_{1/2}^*$	β
0.01($\text{H}_2\text{C}_2\text{O}_4 + \text{NH}_4\text{HC}_2\text{O}_4$)	0.060	0.037	0.080	0.020	0.020	0.017
0.05($\text{NaHC}_4\text{H}_4\text{O}_4$)	0.030	0.027	0.060	0.029	0.030	0.024
0.02($\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$)	0.060	0.040	0.080	0.018		

References

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