# pH* Values of the standard succinate buffer solution in the 50 mass % ethanol—water solvent

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The voltage of a cell without liquid junction consisting of hydrogen electrode, silver/silver chloride reference electrode, and standard succinate buffer solution in the 50 mass % ethanol—water solvent was measured potentiometrically. The measured values of EMF were used for calculating the conventional $pa_{H^*}$ values of the succinate buffer solution. By means of these values the calibration of pH-meter was performed. Furthermore, different buffer solutions and standards in the 50 mass % ethanol—water solvent were used as electrolytes in some types of potentiometric cells the voltage of which was measured in the working pH* scale. The calibration of the measured cell with respect to standard in the mixed solvent was compared with the calibration with respect to the pH standard in water. The pH* values from the working scales were confronted with the pH* values obtained from the concentration pH* scale.

Проводились потенциометрические измерения значений э.д.с. в элементе без перевода с водородным электродом и хлоросеребрянным электродом сравнения для стандартного буферного раствора янтарата в 50 (вес)%-ном этаноле. На основании полученных значений э.д.с. были рассчитаны условные значения $pa_{H^*}$ данного буферного раствора и использованы для калибровки pH-метра. Далее были в разных типах потенциометрических цепей с переводом в рабочей шкале pH* измерены буферные растворы и стандарты в 50 (вес)%-ном растворителе этанол—вода. Была сравнена калибровка измерительного элемента по стандарту в смешанном растворителе с калибровкой по стандарту pH в воде. Значения pH* рабочих шкал были сравнены со значениями pH*, полученными из концентрационной шкалы pH*.

The pH* values of primary standards in the 50 mass % ethanol—water solvent are to be determined in the same way as in the 50 mass % methanol—water solvent [1]. By this method, the citrate [2], phosphate [2], tetraborate [2], salicylate [3], oxalate [3], and some succinate [3] buffer solutions were investigated in the 50 mass % ethanol—water solvent and recommended for the calibration of pH-meter.

For measuring the acidity in the 50 mass % ethanol—water solvent, the working pH* scales as well as the concentration pH* scales are used like in the 50 mass % methanol—water solvent [4].

Our aim was to obtain the defining values $pa_{H^*} = pH^*(S)$ of succinate buffer solution in the 50 mass % ethanol—water solvent and to compare the results of acidity measurements in the 50 mass % ethanol—water solvent obtained by different methods from acidity scales with each other.

## Experimental

### *Purification of solvent and chemicals*

Denaturated alcohol was purified by distillation. The middle fraction 78—79°C was caught. Ethanol of u.v. grade was not purified. The content of water in ethanol was determined by the Fischer method.

Potassium hydrogen phthalate, potassium dihydrogen phosphate, disodium hydrogen phosphate, disodium tetraborate, succinic acid, sodium succinate, potassium chloride, and sodium chloride were purified by recrystallization from aqueous solutions [5]. 5,5′-Diethylbarbituric acid and its sodium salt were purified by the method described in monograph [6] while the purification of lithium hydrogen succinate, salicylic acid, and sodium salicylate was carried out according to paper [3].

### *Measuring equipment*

Silver/silver chloride electrode prepared by thermal-electrolytic method [7].

Commercial calomel electrode, Radiometer K 401.

Hydrogen electrode with Platinum Black [1].

Glass electrode, Radiometer G 202 B.

The defining $pa_{H^*}$ measurements of buffer solutions in the 50 mass % ethanol—water solvent were carried out by the method presented in paper [1]. The pH* measurements of buffer solutions in the cells with liquid junction in the 50 mass % ethanol—water solvent were performed in the same way as in the 50 mass % methanol—water solvent [4].

### *Instruments*

An RFT-DC digital voltmeter (GDR) was used for potentiometric measurements with hydrogen indication electrode. Pure hydrogen was obtained from a generator (General Electric). The temperature was kept constant by means of a thermostat U 10. The barometric pressure was measured with a portable station barometer (GDR).

The EMF measurements with glass indication electrode were carried out with a digital pH-meter pHM-64 (Radiometer).

### *Measuring cells*

Cell A

Pt $|H_2|$ solution S in ethanol—water (50 mass %) |AgCl| Ag

Cell B

Glass electrode | solution X or S || saturated KCl in ethanol—water (50 mass %) |AgCl| Ag

Cell C

Glass electrode | solution X or S || saturated KCl in $H_2O$ $|Hg_2Cl_2|$ Hg

### *Calculation*

The measured defining values of EMF of cell A were used for calculating the $pa_{H^*}$ values according to [1].

The pH* values of the working scale as well as concentration scale were calculated from the EMF values measured with cell B and cell C by the method presented in paper [4].

## Results and discussion

The composition of the measured defining buffer solutions in the 50 mass % ethanol—water solvent is given in Table 1. The measured and corrected values of EMF were used for calculating the values of $pa_{H^+}\gamma^*_{Cl^-}$ and $pa_{H^*}$.

The dependence of the values of $pa_{H^+}\gamma^*_{Cl^-}$ on concentration of the $Cl^-$ ions was processed by linear regression. The numerical value of $p(a_{H^+}\gamma^*_{Cl^-})$ was obtained as the $y$ intercept for the zero relative molality of the $Cl^-$ ions by means of linear regression of the relationship $pa_{H^+}\gamma^*_{Cl^-} = f(m_{Cl^-})$. The value of $p(a_{H^+}\gamma^*_{Cl^-})$ of the succinate buffer solution in the 50 mass % ethanol—water solution at 25°C obtained by linear regression is 5.944 pH units and the value of $pa_{H^*}$ thus calculated is 5.83. The value of $p(a_{H^+}\gamma^*_{Cl^-})$ was calculated as the mean of the values of $pa_{H^+}\gamma^*_{Cl^-}$. The value of $p(a_{H^+}\gamma^*_{Cl^-})$ thus calculated is 6.002 pH units, which means that the resulting value of $pa_{H^*}$ is 5.89.

We attributed the value $pa_{H^*} = pH^*(St) = 5.83$ to this standard buffer solution and used it for the pH* measurements of other buffer solutions in the working scale by using cell B and cell C. Besides this standard buffer solution, we employed other standard buffer solution of the composition 0.01 mol $kg^{-1}$ ($H_2Succ + NaHSucc$) for measurements. The defining $pa_{H^*}$ value of the buffer solution of the composition 0.01 mol $kg^{-1}$ ($H_2Succ + LiHSucc$) was determined by *Levchenko et al.* [3] who obtained $pa_{H^*} = 5.03$ at 25°C. We investigated analogous buffer mixture containing NaHSucc instead of LiHSucc in cell A. These measurements gave the value $pa_{H^*} = pH^*(St) = 5.02$ which is in good agreement with the result presented in

*Table 1*

Values of $p(a_{H^+}\gamma^*_{Cl^-})$ and $pa_{H^*}$ of the NaHSucc buffer solutions in the 50 mass % ethanol—water solvent at 25°C

| Molality of buffer solution | $I$ | $E_{cor}$ | $s_R$ | $^1p(a_{H^+}\gamma^*_{Cl^-})$ | $-\log \gamma^*_{H^*}$ | $pa_{H^*}$ |
|---|---|---|---|---|---|---|
| mol kg$^{-1}$ | mol kg$^{-1}$ | mV | | | | |
| 0.02 NaHSucc + 0.0005 NaCl | 0.0205 | 724.77 | 1.844 | 5.804 | 0.1121 | 5.69 |
| 0.02 NaHSucc + 0.005 NaCl | 0.025 | 674.98 | 1.074 | 5.963 | 0.1212 | 5.84 |
| 0.02 NaHSucc + 0.02 NaCl | 0.040 | 639.61 | 1.303 | 5.967 | 0.1447 | 5.82 |
| 0.02 NaHSucc + 0.03 NaCl | 0.050 | 631.78 | 1.398 | 6.011 | 0.1569 | 5.85 |
| 0.02 NaHSucc + 0.06 NaCl | 0.080 | 617.22 | 1.449 | 6.066 | 0.1844 | 5.88 |

NaHSucc — sodium hydrogen succinate.

paper [3]. In subsequent measurements in the working pH* scale, we used succinate and hydrogen succinate buffer solution with sodium salt as a standard. The pH* values obtained by means of these standard buffer solutions are very near, which indicates a good consistence of the working pH* scale with respect to both standards.

The composition of the investigated buffer solutions as well as the results of three methods of calibration in the 50 mass % ethanol—water solvent obtained as described in [4] is presented in Table 2. The results are statistically processed with 95% probability. The first method involves obtaining of the pH* values in the working scale by means of nonaqueous standards while an aqueous standard is used for calibration in the second method. The solutions of HCl with graduated molality and ionic strength adjusted to a constant value in the 50 mass % ethanol—water solvent are used for calibration in measurements in the concentration scale.

If we compare the pH* values obtained with cell B and cell C with each other, we can see that the pH* values obtained with cell B are more reproducible than those obtained with cell C. That is due to the fact that the salt bridge in cell B of the reference electrode is filled with saturated solution of KCl in the 50 mass % ethanol—water solvent while the salt bridge in cell C contains saturated solution of KCl in water.

The aqueous phosphate buffer solution with $pH = 6.865$ was used as a standard buffer solution in the second method of calibration. The measured values of "pH(X)" were transormed into pH*(X) by means of the correction factor $\delta$ as described in paper [4]. For the 50 mass % ethanol—water solvent we experimentally found the value $\delta = 0.1908$ which is in good agreement with the literature data [8, 9].

The pH* values based on the third method of calibration are obtained in the concentration scale.

The last column of the table contains the data of the defining measurements provided they were made for a certain buffer solution.

We confronted three methods of formation of acidity scales in the 50 mass % ethanol—water solvent. We have found that, like in the 50 mass % methanol—water solvent [4], the acidity measurements in the working pH* scale involving the use of aqueous standards and correction factor $\delta$ are less accurate and correct. The results thus obtained are only a rough estimate of the correct value. The concentration scale also gives less correct and accurate results. Their accuracy is approximately equal to that achieved in the pH* measurements with the correction factor $\delta$. The drawback of this scale consists in the fact that we have to work at a constant ionic strength not only with calibration solutions but also with the measured solutions.

These conclusions are valid up to the ionic strength $I \leq 0.1$ mol kg$^{-1}$. It follows that it is more proper to use the Bates method of calibration of the measuring cell

*Table 2*

Confrontation of different methods of pH* measurements in the 50 mass % ethanol—water solvent at 25°C

| Molality of buffer solution | $I$ | Working pH* scale Nonaqueous standards | | Working pH scale Aqueous standard | Concentration pH* scale HCl standards | | Defining values |
|---|---|---|---|---|---|---|---|
| mol kg$^{-1}$ | mol kg$^{-1}$ | pH*(B) | pH*(C) | pH* = "pH" − $\delta$ | pH*(B) | pH*(C) | $pa_{H^*}$ |
| 0.01 (HSal + NaSal) | 0.01 | 3.88 ± 0.01 | 3.88 ± 0.03 | 4.02 ± 0.08 | 3.79 ± 0.05 | 3.76 ± 0.12 | 3.88[3] |
| 0.01 (HSal + NaSal) + 0.09 NaCl | 0.10 | 3.87 ± 0.01 | 3.87 ± 0.04 | 3.87 ± 0.14 | 3.75 ± 0.08 | 3.73 ± 0.11 | — |
| 0.01 ($H_2$Succ + NaHSucc) | 0.01 | 5.04 ± 0.01 | 5.04 ± 0.02 | 5.16 ± 0.06 | 4.95 ± 0.04 | 4.90 ± 0.12 | 5.03 |
| 0.01 ($H_2$Succ + NaHSucc) + 0.09 NaCl | 0.10 | — | — | 4.96 ± 0.09 | 4.86 ± 0.06 | 4.83 ± 0.10 | 4.97 |
| 0.02 NaHSucc | 0.02 | 5.82 ± 0.01 | 5.82 ± 0.01 | 5.93 ± 0.03 | 5.77 ± 0.04 | 5.72 ± 0.11 | 5.83 |
| 0.02 ($KH_2PO_4$ + $Na_2HPO_4$) | 0.08 | 7.76 ± 0.02 | 7.70 ± 0.03 | 7.77 ± 0.02 | 7.77 ± 0.02 | 7.67 ± 0.09 | — |
| 0.02 ($KH_2PO_4$ + $Na_2HPO_4$) + 0.02 NaCl | 0.10 | 7.75 ± 0.01 | 7.69 ± 0.07 | 7.65 ± 0.06 | 7.64 ± 0.01 | 7.54 ± 0.09 | — |
| 0.01 (TRIS + TRIS − HCl) | 0.01 | 7.61 ± 0.07 | 7.58 ± 0.08 | 7.71 ± 0.09 | 7.51 ± 0.04 | 7.46 ± 0.14 | — |
| 0.01 (TRIS + TRIS − HCl) + 0.09 NaCl | 0.10 | 7.88 ± 0.10 | 7.86 ± 0.13 | 7.83 ± 0.14 | 7.77 ± 0.06 | 7.73 ± 0.12 | — |
| 0.0053 $Na_2B_4O_7$ | 0.0106 | 10.59 ± 0.03 | 10.62 ± 0.04 | 10.61 ± 0.13 | 10.50 ± 0.06 | 10.49 ± 0.12 | 10.60[2] |
| 0.0053 $Na_2B_4O_7$ + 0.0894 NaCl | 0.10 | 10.41 ± 0.06 | 10.40 ± 0.11 | 10.24 ± 0.18 | 10.30 ± 0.03 | 10.26 ± 0.09 | — |
| 0.01 (HDEB + NaDEB) | 0.01 | 8.76 ± 0.01 | 8.75 ± 0.03 | 8.82 ± 0.09 | 8.66 ± 0.03 | 8.62 ± 0.13 | — |
| 0.01 (HDEB + NaDEB) + 0.09 NaCl | 0.10 | 8.75 ± 0.03 | 8.72 ± 0.08 | 8.66 ± 0.07 | 8.63 ± 0.04 | 8.58 ± 0.09 | — |

HSal — salicylic acid; NaSal — sodium salicylate; $H_2$Succ — succinic acid; NaHSucc — sodium hydrogen succinate.
HDEB — 5,5′-diethylbarbituric acid; NaDEB — sodium diethylbarbiturate; TRIS — tris(hydroxymethyl)aminomethanes.

for these solutions. As for solutions with higher ionic strength ($I = 2$—$3$ mol kg$^{-1}$), it is evidently preferable to measure in the concentration scale.

## References

1. Kozáková, E., Cséfalvayová, B., and Thurzo, A., *Chem. Zvesti 34,* 158 (1980).
2. Gorina, M. Yu. and Seregina, L. N., *Elektrokhimiya 8,* 829 (1972).
3. Levchenko, Yu. N., Malkova, E. M., Shevalje, V. I., and Tsarapkina, L. A., *Tr. Metrolog. Inst. SSSR 161,* 19 (1975).
4. Kozáková, E. and Cséfalvayová, B., *Chem. Zvesti 34,* 610 (1980).
5. Čihalík, J., Dvořák, J., and Suk, V., *Příručka měření pH.* (Manual of pH-Measurements.) Nakladatelství technické literatury (Publishing House of Technical Literature), Prague, 1975.
6. Perrin, D. D. and Dempsey, B., *Buffers for pH and Metal Ion Control.* Chapman and Hall, London, 1974.
7. Bates, R. G., *Determination of pH Theory and Practice.* (Russian translation.) P. 248. Khimiya, Leningrad, 1972.
8. Bates, R. G., Paabo, M., and Robinson, R. A., *J. Phys. Chem. 67,* 1833 (1963).
9. Douhéret, G., *Bull. Soc. Chim. Fr. 1967,* 1412.

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