

**Standard potential of the silver/silver chloride electrode
in the 50 mass % mixed solvent acetone—water
Pressure of saturated vapour of water—acetone mixtures and
potentiometric measurements with the cell without liquid junction
in 50 mass % acetone**

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The standard potential of the silver/silver chloride electrode in the 50 mass % mixed solvent acetone—water was determined from potentiometric measurements with a cell without liquid junction at 25°C. Attention has been paid to the preparation and use of the hydrogen electrode in acetone—water mixtures with the content of acetone exceeding 40 mass %.

Путем потенциометрических измерений в элементе без перевода был получен стандартный потенциал хлоросеребряного электрода в смешанном 50 (вес)%-ном растворителе ацетон—вода при 25°C. Уделено внимание приготовлению и использованию водородного электрода в смесях ацетон—вода с содержанием более 40 (вес)% ацетона.

The hydrogen electrode represents a primary standard with respect to which the potentials of other electrodes are compared. At the same time, it behaves as a reversible indication electrode the potential of which is a function of the solvated proton in solution. This fact is used for creation of the acidity scales founded on potentiometric measurements in nonaqueous solvents.

The equilibrium potential of a reaction on hydrogen electrode may be defined either in nonaqueous or mixed medium by the expression which is formally similar to the analogous relationship valid for aqueous medium. The only difference

consists in the standard state to which the activity of the solvated proton a_{H^*} is referred (the asterisk denotes the standard state and in this case, it is the infinitely dilute solution in a given solvent).

The partial pressure of hydrogen at which the measurement is carried out may be calculated from the following equation [1]

$$p_{\text{H}_2}/\text{Pa} = (p_{\text{B}} - p_{\text{s}})/\text{Pa} + \frac{0.4}{1813} (h/\text{mm}) \quad (1)$$

where p_{B} is barometric pressure, p_{s} is the pressure of saturated vapour of solvent in Pa, and h is the dipping depth of the inlet tube of hydrogen into the measured solution in mm.

The water—acetone mixtures do not obey the Raoult law and for this reason the values of saturated vapour pressure of these mixtures must be found experimentally [2, 3].

Sometimes, the hydrogen electrode is not reversible. This case arises especially in media containing reducible compounds. Under certain conditions, acetone belongs into this group of compounds. This fact was confirmed by some authors [2, 4, 5] who performed measurements with the hydrogen electrode in solvents containing 5—40 mass % of acetone. It is interesting that this reduction does not take place in water-free acetone [6] even after 24 h bubbling of solution with hydrogen.

The potentiometric measurements carried out with a cell without liquid junction the construction of which is $\text{Pt}|\text{H}_2|1 \text{ mol kg}^{-1} \text{ HCl in 50 mass \% acetone}|\text{AgCl}|\text{Ag}$ (I) enable us to determine the standard potential of a silver/silver chloride electrode in the solvent of this composition. The known value of standard potential of the reference electrode enables to define the acidity scale in 50 mass % acetone.

The standard potential of the silver/silver chloride electrode and EMF of cell (I) are governed by a relatively complicated expression [2] which, however, may be simplified into the following form

$$E'_0/\text{mV} = {}_sE_{\text{Ag}|\text{AgCl}}^0/\text{mV} - (2KB'/\text{mV}) \cdot [m_{\text{HCl}}/\text{mol kg}^{-1}] \quad (2)$$

The value of E'_0 includes the measured EMF of cell (I) and further terms resulting from the Nernst equation and Debye—Hückel relationship. The values of E'_0 obtained for the solutions of HCl with gradual molality enable us to calculate by the use of linear regression the value of standard potential ${}_sE_{\text{Ag}|\text{AgCl}}^0$ as well as the constant B' .

Experimental

Anal. grade acetone (Lachema, Brno) was purified before use as follows:

The reactivated molecular sieve Potasit 2A (J. Dimitrov Chemical Works, Bratislava) was added into the solvent which was allowed to stand for 24 h. 100 g of molecular sieve were

used for 2 dm³ of the solvent. After 24 h the solvent was distilled through a column of 0.5 m length. For checking the quality of the solvent, the water content was determined by gas chromatography (0.01—0.04 mass %). The density of the solvent was also determined and compared with tabulated values.

Hydrochloric acid was purified by twofold distillation of the constant boiling azeotropic mixture. Its concentration was estimated by titration using water-free Na₂CO₃ as primary standard and controlled gravimetrically as well.

The solutions of hydrochloric acid in 50 mass % acetone in the range 0.002—0.15 mol kg⁻¹ HCl were prepared from the purified solvent and hydrochloric acid. On adding the calculated mass of acid into polyethylene wide-neck bottles, the solvent was poured on and weighed on analytical balance (Sartorius) up to total mass of 1000 g.

The hydrogen electrodes used for potentiometric measurements were prepared as follows:

Hydrogen electrode H 1

It was prepared by electrolytic platinization of a platinum strip in the 2 mass % solution of PtCl₄ in 2 M-HCl at the current density of 20 mA cm⁻². The solution was not stirred and the time period of electrolysis was 10 min.

Hydrogen electrode H 2

It was the so-called "activated" platinum electrode prepared by polishing and short-time dipping of a platinum strip into a solution of aqua regia [2].

Hydrogen electrode H 3

It was prepared by electrolytic deposition of a layer of Pd Black on the surface of a platinum strip in the 2 mass % solution of PdCl₂ in 0.1 M-HCl at the current density of 20 mA cm⁻². The electrolysis proceeded for 10 min in the nonstirred solution.

The silver/silver chloride electrodes prepared by thermoelectrolytic method [7] were used as reference electrodes for potentiometric measurements.

The pressure of saturated vapour of the 50 mass % acetone—water mixture was 22.80 kPa at 25°C. It was found by interpolating the literature data [3].

The potentiometric measurements were performed with a digital voltmeter, type 1652-2 (Hungary). It is accurate to ±0.1 mV within the range of 1 V.

Hydrogen for potentiometric measurements was obtained from a hydrogen generator (General Electric) and was humidified with the measured solution before use. The temperature was held constant during potentiometric measurements by means of a thermostat U 10.

The polarographic measurements were performed with a polarograph OH 105 (Radelkis, Budapest). The 2 M solution of glycine in 1 M-NaOH was used as supporting electrolyte for polarographic measurements. The concentration of acetone was determined by the method of calibration curve from polarographic measurements according to [8].

Results and discussion

In order to achieve correct and reproducible potentiometric measurements, three types of hydrogen electrodes (denoted H 1, H 2, H 3) were examined in cell (I).

The potential of the cell was investigated potentiometrically in the course of its establishment. The values of EMF obtained at 25°C for the cells containing 0.02 mol kg⁻¹ of HCl in 50 mass % acetone as electrolyte with equal reference electrode and different indication electrodes (H 1, H 2, and H 3) are represented as functions of time in Fig. 1.

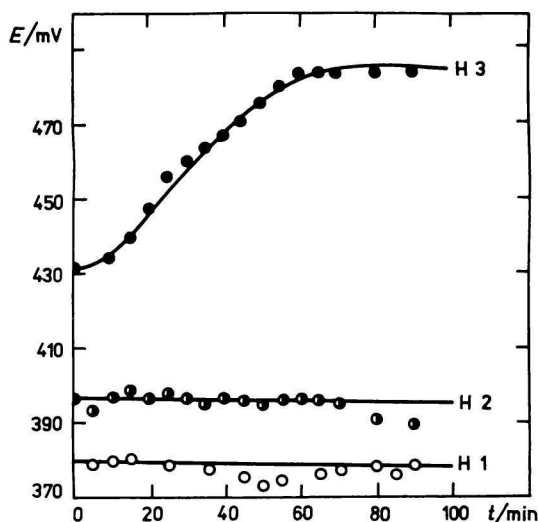


Fig. 1. Establishment of potential in cell I with electrodes H 1, H 2, and H 3.

Simultaneously with potentiometric measurements, some millilitres of electrolyte of cell I were taken in regular time intervals and the content of acetone in these samples was polarographically estimated. The content of acetone in electrolyte of cells I with different types of hydrogen electrode is given as a function of time in Table 1.

It results from potentiometric and polarographic measurements that hydrogen electrode H 3 prepared by electrolytic deposition of Palladium Black on the surface of a platinum strip is the most suited to measurements of the values of EMF of a cell without liquid junction containing the 50 mass % acetone—water mixture.

Table 1

Content of acetone in electrolytes of cell I determined polarographically for different hydrogen electrodes as a function of time
Mass % of acetone (w) in the time t

Electrode	t/s					
	0	1200	2400	3600	4800	6000
$w/\text{mass \%}$						
H 1	50.00	48.19	—	47.73	—	46.67
H 2	50.00	49.16	48.40	46.55	46.06	38.84
H 3	50.00	50.00	50.00	50.00	—	50.00

Feakins and Tomkins [9] who selected hydrogen electrode for potentiometric measurements in the 90 mass % methanol—water mixture came to similar conclusions. On the basis of measurements of the EMF values of cell (I) without liquid junction, the standard potential of the silver/silver chloride electrode in the mixed acetone—water solvent was determined. The measured values of EMF are the mean of six values found for each molality of HCl. They were obtained from measurements with six independent pairs of electrodes (two indication electrodes and three reference electrodes). The mean values of EMF as well as the values of E'_0 calculated by means of eqn (2) for the molality of HCl ranging from 0.002 mol kg^{-1} to 0.015 mol kg^{-1} are given in Table 2.

By using linear regression of the relation $E'_0 = f(m_{\text{HCl}})$ and the convention for effective diameter of the chloride ion in the Debye—Hückel equation, *i.e.* $a^0 = 4.30 \times 10^{-10}$ m, the following results were obtained: The standard potential ${}_sE'_{\text{Ag}|_{\text{AgCl}}}$ in the 50 mass % acetone—water solvent at 25°C is equal to 163.77 mV, $r_c = 0.9882$, and $2KB' = 91.772$ mV.

Table 2

Values of EMF and E'_0 of cell I for varying molality of HCl in the 50 mass % acetone—water mixture at 25°C

Molality of HCl mol kg^{-1}	E/mV	E'_0/mV
0.002	484.2	164.00
0.005	440.6	164.75
0.007	420.1	160.39
0.010	407.5	164.58
0.015	389.3	165.22

The value of standard potential of the silver/silver chloride electrode in the mixed 50 mass % acetone—water solvent obtained by us is in good agreement with the values of ${}_sE_{\text{Ag}|\text{AgCl}}^0$ found for other contents of acetone which are listed in Table 3. This table also contains the values of relative permittivity ϵ_r of acetone—water mixtures.

Table 3

Standard potentials of the silver/silver chloride electrode in acetone—water mixtures at 25°C

w/mass %	ϵ_r	${}_sE_{\text{Ag} \text{AgCl}}^0/\text{mV}$
5		219.00 [2]
10	73.02	215.60 [2]
20	66.98	207.90 [2], 207.90 [10]
40	54.60	186.00 [10], 185.90 [2]
50	48.22	163.77
60	41.80	147.00 [10]
80	29.62	60.00 [10]
100		-325.00 [10]

By using linear regression of the values of ${}_sE_{\text{Ag}|\text{AgCl}}^0$ within the range of acetone percentage 10—60 mass %, we obtained the following expression for the relationship between ${}_sE_{\text{Ag}|\text{AgCl}}^0$ and percentage of acetone in these acetone—water mixtures

$${}_sE_{\text{Ag}|\text{AgCl}}^0/\text{mV} = 229.87 - 1.297 x/\text{mass \%}$$

The symbol x stands for the percentage of acetone, the correlation coefficient being $r_c = -0.985$.

The value of the standard potential of the silver/silver chloride electrode calculated from this equation is ${}_sE_{\text{Ag}|\text{AgCl}}^0 = 165.00$ mV which is in good agreement with the value found experimentally at 25°C (163.77 mV).

Ságnér and Pechová [11] recommended to use the linear relationship between the values of relative permittivity of a mixture and its composition for calculating the values of standard potential of the silver/silver chloride electrode in ethanol—water mixtures (in the range 10—70 mass % of ethanol).

Similar relation valid for acetone—water mixtures may be expressed by the equation

$${}_sE_{\text{Ag}|\text{AgCl}}^0/\text{mV} = 310.33 - \frac{6893}{\epsilon_r}$$

the correlation coefficient being $r_c = -0.997$.

The value of standard potential calculated for the 50 mass % acetone—water mixtures from this equation is 167.39 mV. This value is not in so good agreement with the experimental value as the value calculated from the preceding equation.

The value of standard potential of the silver/silver chloride electrode thus obtained is a basis for other potentiometric measurements with a cell without liquid junction necessary for defining the acidity scale in the mixed 50 mass % acetone—water solvent.

References

1. Hills, G. J. and Ives, D. J. G., *Nature* 163, 997 (1949).
2. Feakins, D. and French, C. M., *J. Chem. Soc.* 1956, 3168.
3. Beare, W. G., *J. Phys. Chem.* 34, 1310 (1930).
4. Moore, A. and Felsing, R., *J. Amer. Chem. Soc.* 69, 1076 (1947).
5. Foresti, M., *Atti XXVII Riunione Bologna Soc. Ital. Progr. Sci.* 5, 346 (1939).
6. Evereth, D. H. and Rasmussen, S. E., *J. Chem. Soc.* 1954, 2812.
7. Paabo, M., Robinson, R. A., and Bates, R. G., *Anal. Chem.* 38, 1573 (1966).
8. Zuman, P., *Collect. Czech. Chem. Commun.* 15, 839 (1950).
9. Feakins, D. and Tomkins, R. P. T., *J. Chem. Soc.* A1967, 1458.
10. de Ligny, C. L., Bax, D., Alfenaar, M., and Mohr, N. J., *Rec. Trav. Chim. Pays-Bas* 91, 601 (1972).
11. Ságner, P. and Pechová, H., *Sborník vědeckých prací Vysoké školy chemicko-technologické.* (Collected Papers of the Institute of Chemical Technology.) P. 51. Pardubice, 1970.

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