Influence of composition of the methanolic-aqueous solvent on properties of the cadmium and chloride ion-selective electrode

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Dedicated to Professor Ľ. Treindl, DrSc., in honour of his 60th birthday

The influence of methanolic-aqueous solvent ($x_{CH_3OH} = 0.1—0.8$) on electromotive voltage of the galvanic cell consisting of a cadmium or chloride ion-selective electrode and a saturated calomel electrode has been studied. The electrode potential of the cadmium ion-selective electrode is linearly dependent on composition of the solvent for the solution of 10^{-2} M--Cd(ClO$_4$)$_2$ and is governed by the following equation

$$E_{Cd}^{ISE} = 96.5 + 131.5\, x_{CH_3OH}$$

By the method of least squares the standard electrode potentials of the cadmium ion-selective electrode have been calculated. They are linearly dependent on composition of the solvent as follows

$$E_{Cd}^{\circ} = 144.8 + 113\, x_{CH_3OH}$$

The dependence of the standard Gibbs energy of transport of the cadmium ion from water into methanolic-aqueous solvent at 298 K can be expressed by the following equation

$$\Delta G_{tr}^{\circ} = 27.9 - 192.3\, E_{m}^{\circ}$$

where E_{m}° is standard electrode potential in a given binary solvent. The Gibbs energy of transport increases with the content of methanol in the solvent.

Изучалось влияние сложного растворителя метанол—вода состава ($x_{CH_3OH} = 0.1—0.8$) на Э.Д.С. гальванической цепи включающей кадмийселективный или хлоридселективный электрод и насыщенный каломельный электрод. Потенциал Cd-СЭ зависит от состава растворителя линейно. В растворе 10^{-2} M-Cd(ClO$_4$)$_2$ его значение выражает отношение

$$E_{Cd}^{ISE} = 96,5 + 131,5\, x_{CH_3OH}$$

Методом наименьших квадратов были рассчитаны стандартные электродные потенциалы Cd-СЭ. Они линейно зависят от состава растворителя

$$E^{\circ}_{\text{Cd}} = 144{,}8 + 113\, x_{\text{CH}_3\text{OH}}$$

Зависимость стандартной свободной энтальпии переноса Cd^{2+}-ионов из воды в растворитель метанол—вода при температуре 298 К описывает выражение

$$\Delta G^{\circ}_{\text{tr}} = 27{,}9 - 192{,}3\, E^{\circ}_{\text{m}}$$

где E°_{m} стандартный электродный потенциал в данном бинарном растворителе. Свободные энтальпии переноса растут с содержанием метанола в растворителе.

The application of nonaqueous and mixed solvents in ionometry considerably extends the use of ion-selective electrodes in practice. The most appropriate electrodes for measurements in such solvents are electrodes with solid membrane [1—4]. The potentiometric measurements in these systems may also be used for studying the thermodynamics of the solutions of electrolytes [5, 6]. This paper is concerned with investigations of the electrochemical properties of the cadmium and chloride electrodes in methanolic-aqueous solvents and with their use for studying the solutions of electrolytes.

Experimental

The calibration solutions for verifying the function of the cadmium ion-selective electrode were prepared by dissolving 3.0848 g of anal. grade crystalline cadmium nitrate in 100 cm³ of deionized water (conductivity $G < 1\ \mu\text{S}$). By diluting the stock solution, the calibration solutions were obtained in the concentration interval 10^{-1}—10^{-5} mol dm⁻³. In a similar way the calibration solutions of potassium chloride were prepared for calibrating the chloride ion-selective electrode. The content of methanol in the binary methanol—water solvents expressed by mole fraction did not exceed the value of 0.8 ($x_{\text{CH}_3\text{OH}} = 0.1$—0.8). The solutions of 10^{-2} mol dm⁻³ concentration were obtained by weighing the corresponding salt and dissolving it in 100 cm³ of a given binary solvent. The solutions of 10^{-3}—10^{-4} mol dm⁻³ concentration were prepared by dilution. The ionic strength of solutions was equal to 0.3 mol dm⁻³. It was held constant by means of anal. grade sodium perchlorate. The voltage of the cell consisting of a cadmium or chloride ion-selective electrode (CRYTUR, Monocrystals, Turnov) and a reference saturated calomel electrode (CRYTUR RCE-101 or 102 with doubled salt bridge) was measured on a digital pH-meter MS-11 (Laboratorní přístroje, Prague) within accuracy ± 1 mV. All measurements were carried out in a closed thermostated vessel EA 876-20 T (Metrohm, Switzerland) at the temperature of (298 ± 0.1) K held constant by means of a thermostat. The solution was stirred during measurements.

Results and discussion

The establishment of voltage of the cell consisting of an ion-selective electrode and a saturated calomel electrode depends on the concentration of elec-

trolyte and the content of methanol in the solvent. The increase in methanol content or the decrease in electrolyte concentration results in an increase in the time of establishment. The maximum time of establishment was 15 min.

The dependence of electromotive voltage of the cell on concentration of the cadmium ions (10^{-2}—10^{-4} mol dm^{-3}) and composition of the solvent is linear (Fig. 1, Table 1). The slope of this dependence varies from 28 mV for aqueous solution to 25 mV for methanolic-aqueous solution ($x_{CH_3OH} = 0.75$). The increase in methanol content of the solvent is accompanied by an increase in electromotive voltage of the cell. The maximum increase in electromotive voltage when compared with aqueous solution was observed for methanolic-aqueous solution with $x_{CH_3OH} = 0.8$ and was equal to 31 mV. These data are in agreement with paper [7].
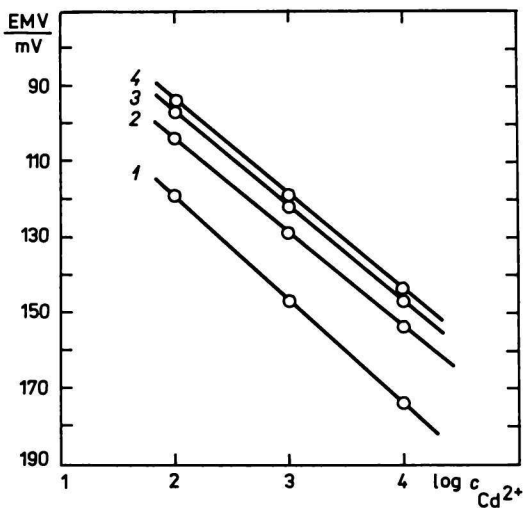

Fig. 1. Dependence of electromotive voltage (EMV) on concentration of the cadmium ions in methanolic-aqueous solutions of varying composition at 298 K.
1. $x_{CH3OH} = 0.0$, *2.* $x_{CH3OH} = 0.25$, *3.* $x_{CH3OH} = 0.5$, *4.* $x_{CH3OH} = 0.75$.

Table 1

Constants of the equation of straight line expressing the dependence of electromotive voltage of the cell consisting of cadmium ion-selective and saturated calomel electrode on composition of the solvent

$$E = A + B x_{CH3OH}$$

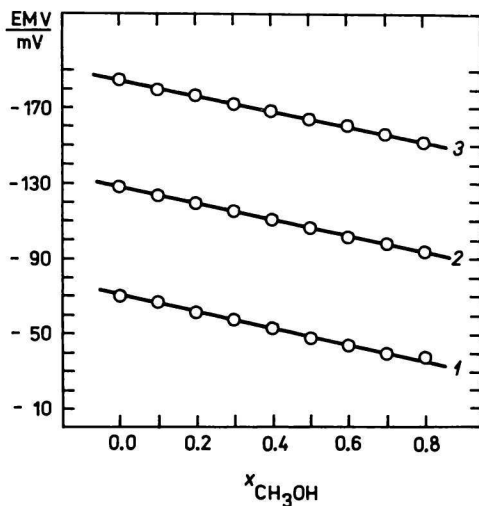| $c(Cd^{2+})$/(mol dm^{-3})	10^{-2}	10^{-3}	10^{-4}
A	− 149.0	− 176.9	− 199.7
B	38.5	38.2	37.6
r	0.999	0.999	0.998
s	0.300	0.524	0.534

r — correlation; s — standard deviation.

Fig. 2. Variation of electromotive voltage with composition of the solvent (methanol—water) and concentration of the chloride ions at 298 K.
1. $c(Cl^-) = 10^{-2}$ mol dm^{-3};
2. $c(Cl^-) = 10^{-3}$ mol dm^{-3};
3. $c(Cl^-) = 10^{-4}$ mol dm^{-3}.

The electromotive voltage of the cell containing a chloride ion-selective electrode and a reference electrode RCE 102 increases with decreasing concentration of the chloride ions. The increase in methanol content in solvent reduces the values of electromotive voltage (Fig. 2). This dependence is linear

$$E = A + B x_{CH_3OH}$$

The constants A and B of this equation were calculated for individual concentrations of the chloride ions (10^{-2}—10^{-4} mol dm^{-3}) and are given in Table 2. The calculated values of electromotive voltage are in very good agreement with the experimental results.

The electrode potentials of the cadmium ion-selective electrode in individual binary solvents were calculated from the corresponding electromotive voltage and from the calculated electrode potentials of the saturated calomel electrode [8]. The electrode potential of the cadmium ion-selective electrode (E_{Cd}^{ISE}/mV) is linearly dependent on composition of the solvent. For 10^{-2} mol dm^{-3} concentration of the cadmium ions it holds

$$E_{Cd}^{ISE} = 96.5 + 131.5 x_{CH_3OH}$$

the correlation and standard deviation being 0.997 and 2.9, respectively.

Provided no interfering ions are present in the solution, the potential of the cadmium ion-selective electrode is determined by activity of the cadmium ions according to the following equation

$$E_{Cd}^{ISE} = E^\circ + \frac{RT}{2F} \ln \gamma_\pm c$$

Table 2

Constants of the equation of straight line expressing the electromotive voltage of the cell consisting of chloride ion-selective and saturated calomel electrode

$c(Cl^-)/(mol\ dm^{-3})$	10^{-2}	10^{-3}	10^{-4}
A	69.7	127.9	184.6
B	−43.2	−44.5	−42.3
r	0.998	0.999	0.999
s	0.942	0.335	0.817

Table 3

Mean activity coefficients $\gamma_{\pm}$ and standard potential of the cadmium ion-selective electrode $E^{o'}$

x_{CH_3OH}	$c(Cd^{2+})/(mol\ dm^{-3})$			$E^{o'}/mV$
	10^{-2}	10^{-3}	10^{-4}	
0	0.7104	0.8858	0.9609	144
0.1	0.6890	0.8759	0.9573	159
0.2	0.6652	0.8646	0.9532	173
0.3	0.6380	0.8513	0.9483	185
0.4	0.6074	0.8358	0.9424	196
0.5	0.5726	0.8175	0.9355	207
0.6	0.5328	0.7955	0.9269	218
0.7	0.4846	0.7674	0.9157	230
0.8	0.4352	0.7364	0.9030	239

while the mean activity coefficient $\gamma_{\pm}$ (Table 3) is defined by the Debye—Hückel relationship [9]

$$-\log \gamma_{\pm} = A|z_+ z_-| I^{1/2}/(1 + Ba^o I^{1/2})$$

where z is the charge number of ion, I is ionic strength and

$$A = 1.82481 \times 10^6 (\varepsilon T)^{-3/2}\ dm^{3/2}\ mol^{-1/2}\ K^{3/2}$$
$$B = 502.90 (\varepsilon T)^{-1/2}\ dm^{3/2}\ mol^{-1/2}\ K^{1/2}\ nm^{-1}$$
$$a^o = 0.33\ nm$$

The relative permittivity of binary solvent ε_{AW} was calculated for individual compositions by using the expression [7]

$$\varepsilon_{AW} = \varepsilon_W - (\varepsilon_W - \varepsilon_A) x_A$$

where ε_{AW}, ε_W, ε_A, and x_A are relative permittivity of alcoholic-aqueous solution, relative permittivity of water, relative permittivity of alcohol, and mole fraction of alcohol, respectively.

The dependence of potential of the cadmium ion-selective electrode on relative permittivity (concentration of the cadmium ions 10^{-2} mol dm^{-3}) is linear and has the form

$$E_{Cd}^{ISE} = 825.1 - 381.9 \log \varepsilon_{AW} \quad \text{at } T = 298 \text{ K}$$

The correlation is 0.997 and the standard deviation is equal to 3.16.

The increase in content of methanol in binary solvent reduces the mean activity coefficient. The apparent standard electrode potential of the cadmium ion-selective electrode $E^{o\prime}$ calculated by the method of least squares increases (Table 3). The dependence of $E^{o\prime}$ on solvent composition is linear

$$E^{o\prime} = 144.8 + 113 \, x_{CH_3OH}$$

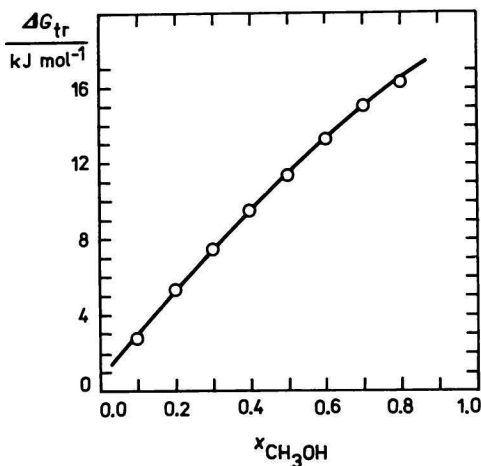the correlation and standard deviation being 0.999 and 1.23, respectively.

Fig. 3. Dependence of the Gibbs energy of transport on composition of the solvent (methanol—water) at 298 K.

On the basis of the determined standard potentials the standard Gibbs energies of transport have been calculated [10]

$$\Delta G_{tr}^{o} = nF(E_{H_2O}^{o\prime} - E_{m}^{o})$$

where $E_{H_2O}^{o\prime}$ is standard electrode potential in water, E_{m}^{o} standard electrode potential in a given binary solvent, and n the number of elementary charges. Under given conditions it is valid at 298 K

$$\Delta G_{tr}^{o} = 27.9 - 192.3 \, E_{m}^{o}$$

The overall effect of medium can be expressed by the Gibbs energy of transport ΔG_{tr} for which it holds

$$\Delta G_{\text{tr}} = \Delta G_{\text{tr}}^{\circ} + nRT \ln \gamma_{\pm}^{\text{H}_2\text{O}}/\gamma_{\pm}^{\text{m}}$$

The increase in methanol content in binary solvent brings about increase in the Gibbs energy of transport (Fig. 3).

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