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Direct evidence of concentration and potential profiles in the electrolyte diode

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Abstract

Electrolyte diode is an electrochemical microsystem showing complex nonlinear behaviour due to interactions of diffusion, migration and chemical reactions. In our recent works we have developed a mathematical model of the electrolyte diode which predicted steep concentration and potential profiles on a spatial interval of several micrometers in the closed mode. The main aim of this work is the experimental verification of the concentration and potential profiles predicted by the model. In this work two techniques for direct observation of spatial concentration and potential profiles in the electrolyte diode are presented. Two different methods were used: (i) visualization of the acid–base boundary using acid–base indicators and (ii) direct measurements of electric potential profiles using the array of microelectrodes. As the presence of an indicator changes the properties of the system, there is a good agreement between modelling and experimental results only at relatively low values of external potential difference. Results of the other method confirm the model predictions in broad range of external potential difference values.

Keywords: Electrolyte diode; Electrochemical microsystems; Acid–base equilibria

1. Introduction

The electrolyte diode is a system consisting of two electrolyte reservoirs (in our case, one containing HCl solution, the other containing KOH solution) separated by a permeation layer (membrane) or by a capillary (microchannel) suppressing the convective flow, while the diffusion and migration flows can pass through. When an external electric field is connected in a proper way, diode-like action can be observed [1]. In the open mode, potassium and chloride ions are driven into the permeation layer, forming a zone of relatively high conductivity with high current density proportional to the potential difference of the external electric field (cf. Figs. 1a and 3a–h). Almost linear profiles of concentrations and of electric potential are established and the behaviour of the system is similar to that of a spatially homogeneous conducting layer. When the polarity of the external electric field is reversed (cf. Fig. 1b), a narrow zone of almost pure water is formed in the permeation layer; the conductivity is very low there (cf. Fig. 3m–t).

Typical experimental current-voltage characteristics similar to those of a semiconductor diode is shown in Fig. 2a, typical time course of the electric current during measurement of the current-voltage characteristics can be seen in Fig. 2b. The convention used in this work is that the KOH and HCl reservoirs are on the left-hand side and the right-hand side, respectively, as it can be seen in Fig. 1. Thus, the negative values of the external electric potential difference (defined as $U = \phi^{\mathrm{right}} - \phi^{\mathrm{left}}$) mean that the diode is in the open mode ($U < 0$) and vice versa.

As a combination of two electrolyte diodes, an electrolyte transistor has been constructed [2]. Nonlinear behaviour (oscillations, bistability) has been observed in both systems [3].

The function of the electrolyte diode can be verified by measurement of current-voltage characteristics. The current-voltage characteristics gives us only integral information about the behaviour of the system inside the permeation layer, for more detailed studies we would need to know the profiles inside the permeation layer.

2. Mathematical modelling

In our previous studies [4,5] we have presented the mathematical model suitable also for description of the electrolyte diode. We have developed two versions of the model, using different assumptions. All modelling results mentioned in this paper are obtained from the "non-equilibrium" model where finite rates of the water dissociation and recombination reactions are con-

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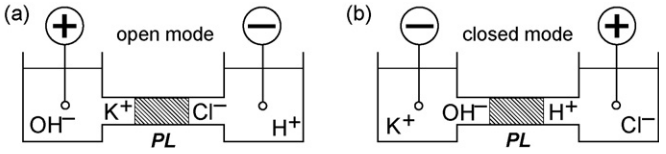

Fig. 1. Principle of the electrolyte diode; the two different regimes – the open (a) and the closed mode (b) – are shown. The permeation layer (PL) is hatched.

sidered. The local electroneutrality assumption is not used here. For a detailed discussion of the model please cf. our papers [4,5], another application of the model has been presented in [6].

The non-equilibrium model (in spatially one-dimensional form as used in this work) consists of mass balances of all ionic components present in the system (K^+, Cl^-, H^+, OH^-):

$$\frac{\partial c_{K^+}}{\partial t} = -\frac{\partial}{\partial x}\left(-D_{K^+}\frac{\partial c_{K^+}}{\partial x} - D_{K^+}c_{K^+}\frac{\partial \phi}{\partial x}\frac{F}{RT}\right) \tag{1}$$

$$\frac{\partial c_{Cl^-}}{\partial t} = -\frac{\partial}{\partial x}\left(-D_{Cl^-}\frac{\partial c_{Cl^-}}{\partial x} + D_{Cl^-}c_{Cl^-}\frac{\partial \phi}{\partial x}\frac{F}{RT}\right) \tag{2}$$

$$\frac{\partial c_{H^+}}{\partial t} = -\frac{\partial}{\partial x}\left(-D_{H^+}\frac{\partial c_{H^+}}{\partial x} - D_{H^+}c_{H^+}\frac{\partial \phi}{\partial x}\frac{F}{RT}\right) - r_1 \tag{3}$$

$$\frac{\partial c_{OH^-}}{\partial t} = -\frac{\partial}{\partial x}\left(-D_{OH^-}\frac{\partial c_{OH^-}}{\partial x} + D_{OH^-}c_{OH^-}\frac{\partial \phi}{\partial x}\frac{F}{RT}\right) - r_1 \tag{4}$$

and of the Poisson's equation for the electric potential profile evaluation

$$\frac{\partial^2 \phi}{\partial x^2} = -\frac{q}{\varepsilon} = -\frac{F}{\varepsilon}(c_{H^+} - c_{OH^-} + c_{K^+} - c_{Cl^-}) \tag{5}$$

Here $c_i(t, x)$ is the concentration of the ith component, t is the time, x is the spatial coordinate, D_i is the diffusion coefficient of the ith component, $\phi(t, x)$ is the electrostatic potential, q is the electric charge density, F is the Faraday's constant, R is the molar gas constant, T is the absolute temperature, ε is the permittivity, respectively.

The symbol r_1 stands for the reaction rate of water dissociation $H^+ + OH^- \leftrightarrow H_2O$:

$$r_1 = k_1(c_{H^+}c_{OH^-} - K_W), \tag{6}$$

here k_1 is the reaction rate constant of the water recombination, K_W is the equilibrium constant of the water dissociation.

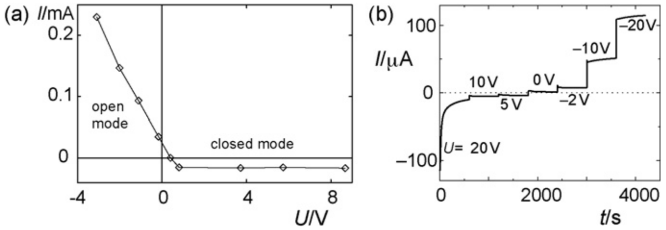

Fig. 2. (a) Typical experimental current-voltage characteristics of the electrolyte diode. (b) The dynamics of the diode: after change of the external electric potential difference, a new stationary state (characterized by constant value of the electric current passing through the system in this figure) is established usually within a few minutes except the initial change (from 0 to 20 V).

We have used the following set of parameters: concentrations of both HCl and KOH in the reservoirs are equal to 0.1 M. Diffusion coefficients of ionic components we have used correspond to the values in dilute aqueous solutions: $D_{H+} = 9.31 \times 10^{-5}\,cm^2\,s^{-1}$, $D_{OH-} = 5.28 \times 10^{-5}\,cm^2\,s^{-1}$, $D_{K+} = 1.96 \times 10^{-5}\,cm^2\,s^{-1}$, $D_{Cl^-} = 2.03 \times 10^{-5}\,cm^2\,s^{-1}$. The value of Faraday constant $F = 96484.56\,C\,mol^{-1}$, the gas constant $R = 8.314\,J\,mol^{-1}\,K^{-1}$. Water product (equilibrium constant) $K_W = 10^{-14}\,M^2$, the rate constant of water recombination $k_1 \cong 1.3 \times 10^{11}\,M^{-1}\,s^{-1}$. The dielectric constant $\varepsilon = \varepsilon_0\varepsilon_r$, where ε_0 is the permittivity of vacuum ($\varepsilon_0 = 8.854 \times 10^{-12}\,C^2\,J^{-1}\,m^{-1}$) and $\varepsilon_r = 78.5$ is the relative permittivity of water.

In a general case we have a set of five partial differential equations (PDEs) of which four are of a parabolic type (mass balances) and one is of an elliptic type (the Poisson equation). In stationary simulations the accumulation term in parabolic equations is equal to zero and thus the set of five elliptic PDEs represents the description of the system. The profiles presented in this paper are results of stationary simulations. Constant values of the electric potential and constant concentrations of both electrolytes are used as the boundary conditions, linear profiles of system variables (concentrations, electric potential) are used as the initial estimate.

The simulation results (cf. Fig. 3) have shown steep gradients of concentrations, potential, charge density and other characteristic quantities (changes of several orders of magnitude) on a spatial interval of several micrometers (also called the acid–base boundary, cf. Fig. 4) when the diode is in the closed mode. This makes the numerical solution of the model equations rather difficult. The model then can be used for description of a broad class of ionic systems, where dissociation reactions, diffusion and migration take place simultaneously, inducing complex nonlinear effects.

An approximate analytical solution has been also derived recently [3,7]. In this case, the diode is divided into three zones (alkaline, neutral and acidic) and the profiles are calculated for each zone apart, using the quasielectroneutrality and quasiequilibrium assumptions [7].

The main aim of this work is qualitative experimental verification of the simulation results. The quantitative comparison would require much more sophisticated model with even more difficult numerical solution. Among others, the quantitative model should take into account changes of diffusion coefficients of ions in the permeation layer with increasing gel density (cf., e.g., [10]), effects of ionic strength, interactions with fixed charges contained in the gel or at the walls of the channel, electrode reactions, etc.

We have developed and tested an experimental device for measuring the electric potential profile inside the electrolyte diode. For verification of the concentration profiles, absorbance pH indicators were used to visualize the changing concentration of H^+ and OH^- ions along the electrolyte diode.

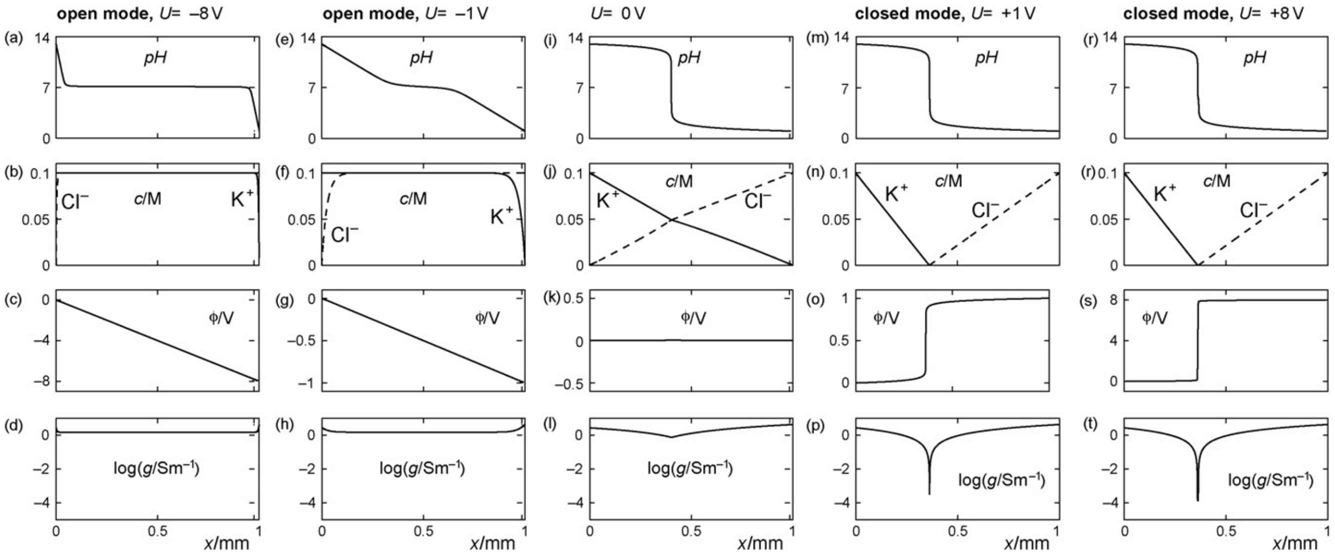

Fig. 3. Computed profiles of pH, concentrations of K^+ and Cl^- ions, electric potential ϕ, and logarithm of conductivity log(g) for external potential differences $U = -8$ and -1 V in the open mode (a–d, e–h, respectively), $U = 0$ V (i–l), and $U = +1$ V and $U = +8$ V in the closed mode (m–p, r–t, respectively).

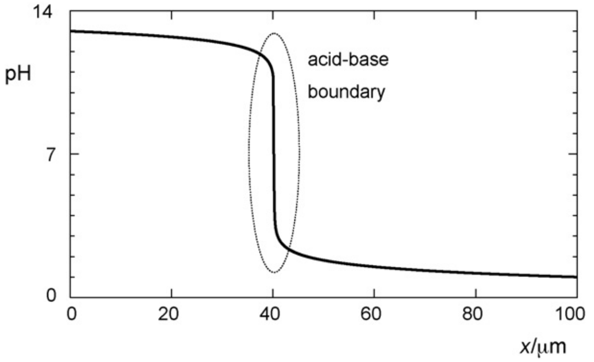

Fig. 4. Computed profile of pH (defined as $-\log_{10}[H^+]$) in the closed mode for the electrolyte diode of the total length 100 μm for boundary concentrations of HCl and KOH equal to 0.1 M and $U = 1$ V.

3. Experimental setup

3.1. Device A: Electrolyte diode in a tubular microreactor

There are various possibilities of the experimental realization of the electrolyte diode, some of them have been published by Noszticzius and co-workers [1]. For experiments with acid–base indicators presented in this work we have developed a tubular microreactor made from Tygon tubing, where the permeation layer has been made from a cylinder-shaped hydrogel (dimensions $W \times L$ were 100–450 μm × 2–3 mm, i.e., the crossflow area between 1×10^{-8} and 1×10^{-7} m^2 approximately) as it can be seen in Fig. 5. Fresh electrolyte solutions are introduced to the inner tube, then the electrolyte passes to the surface of the permeation layer and finally, the electrolyte is led out of the device, as denoted by the arrows.

Relatively low volume of the permeation layer, comparing to the traditional experimental setup of Noszticzius and co-workers [1], means lower residence time of the electrolyte and shorter time necessary to reach the steady state. Concentrations of both the KOH and HCl solutions used were 0.1 M. The platinum wires were used both as measuring and working electrodes in all experiments, using the four-electrodes setup. The electrolyte is fed via a thin PTFE tube, using the ISMATEC peristaltic pump.

As the separating layer mostly the poly-vinyl-alcohol (PVA) gel has been used as it has good mechanical properties, good stability both in acidic and alkaline solutions, high transparency and the lowest fixed charge from the common hydrogels. The PVA gel has been prepared accordingly to the recipe published by Noszticzius and co-workers [1] in the two steps: (i) the stock solution (approximately 30%, w/w of PVA in water) has been prepared from the monomer of nominal molecular weight 31,000 (Fluka order No. 81381), (ii) 2 ml of glutardialdehyde solution (1%, w/w, prepared from the stock Fluka order No. 49630) and 1 ml of 5 M HCl solution have been added to 4 g of the PVA stock solution under continuous stirring. The polymerization is rather fast, the gel should be put into a form within 30 s after mixing. The polymerized gel can be dried out and kept in the dry state for a long time. The dry gel piece is then inserted into the device, and when the water is added, the gel swells and its original volume is restored. Before experiment, the gel plug is washed with 1 M KOH solution to neutralize remaining acidic groups fixed in the polymer chain. For some experiments we have used also the Agar gel as its preparation is easier. The 4% (w/w) agar solution is heated under continuous stirring to its boiling temperature. The gel solidifies as the temperature decreases, yet liquid solution of

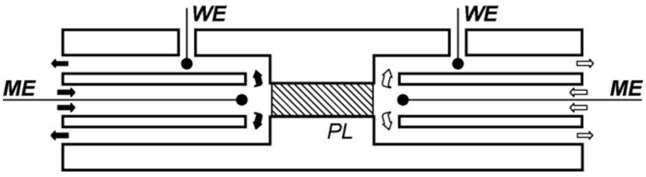

Fig. 5. Electrolyte diode as the tubular microreactor. The hatched part is the permeation layer (PL), measuring electrodes (ME) are located in the inlets of fresh electrolytes, working electrodes (WE) are placed in the electrolyte outlets.

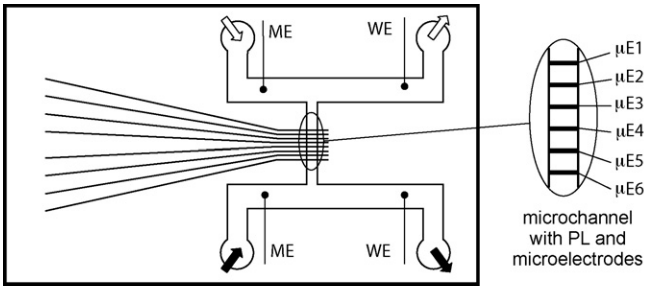

Fig. 6. Scheme of the electrolyte diode with a set of measuring microelectrodes (μE) in the central microchannel with permeation layer (PL). In the experimental Device B eight measuring microelectrodes has been used. Additional pair of measuring (ME) and one pair of working (WE) electrodes are placed in the electrolyte inlets and outlets, respectively.

the gel is introduced into a form. Similarly to the PVA gel, the Agar gel can be dried out and after inserting to its location inside the experimental apparatus it swells in the presence of water to its original volume. This device has been used for experiments with acid–base indicators.

3.2. Device B: Electrolyte diode with electrode array in the permeation layer

For other type of experiments we have developed an alternative construction of the electrolyte diode (cf. Fig. 6). The central microchannel with the permeation layer was approximately 250 μm wide, 400 μm deep and 2–3 mm long. Whole device is fabricated by micro-milling from polystyrene wafers. After fabrication of the channels, the individual plates are connected by thermal bonding. Platinum wires are used both as the working and measuring electrodes. For the measurements of the potential profile at the electrolyte diode, the central microchannel is equipped with additional microelectrodes (Pt wires with diameter of 100 μm) in the distance of 300–400 μm from each other. The device B has been used for measurements of electric potential distribution.

3.3. Supplementary experimental equipment

In both electrolyte diode arrangements described above the electrolytes have been pumped to the inlet channels from reservoirs by a peristaltic pump. Keithley source meter model 2400 was used as the external voltage source, Keithley multimeter model 2700 was used for measurement. Both devices were connected to a computer via GPIB interface. Whole process was controlled by a specially developed subroutine under Matlab environment (cf. Fig. 7). For optical observation of the central part of the diode in some experiments, the microscope Olympus BX51WI has been used. Computer-controlled digital camera Olympus C5050Z has been attached to the microscope. The camera is capable to take high-resolution images automatically in preset intervals down to 5 s.

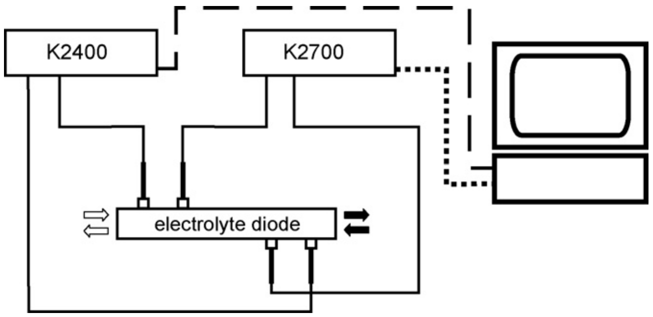

Fig. 7. Connection of the electrolyte diode to the electrolyte inlets and outlets (white and black arrows), potential source (K2400) and multimeter (K2700).

4. Experimental results

4.1. Measuring of the potential course

Experimental course of electric potential has been measured in the diode (Device B) with permeation layer (gel plug) approximately 2.1 mm long which has been equipped with set of eight platinum microelectrodes (cf. Fig. 6). In the open mode, the potential profile is almost linear (Fig. 8a) as it has been predicted by the model (cf. Fig. 3c and g). The major part of the total potential change in the closed mode can be observed left to the central part of the diode (Fig. 8b). The potential profiles predicted by the model are similar (cf. Fig. 3o and s). Experimental results qualitatively correspond well to the model predictions. Quantitative variations can be found as the model does not include the effects of the gel permeation layer on transport of ions.

4.2. Visualization of the acid–base boundary

The steep change of pH inside the electrolyte diode in the closed mode led to the idea to use an acid–base indicator and observe its absorbance change under a microscope. There are several limitations for the choice of a suitable indicator: (i) it should have a distinct colour, absorbance or fluorescence change, in an ideal case between pH 6 and 8, (ii) it should be well soluble both in acidic and alkaline solutions, and (iii) it should not be rapidly washed out of the gel. Also the concentration of the dye should be as low as possible as the ionic forms of indicators can affect the behaviour of the electrolyte diode. Possible problems with the use of an acid–base indicator are, e.g., the dependency of the indicator behaviour on the ionic strength and washing-out of the indicator out of the permeation layer of the electrolyte diode [8].

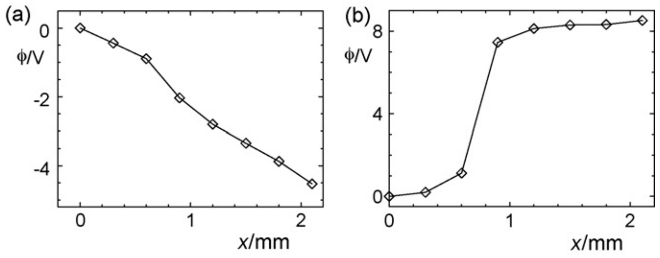

Fig. 8. Potential course in the electrolyte diode (a) in the open mode, (b) in the closed mode.

Preliminary experiments have shown that the most suitable (although still not ideal) indicators for our purposes are congo red and thymol blue. Congo red possesses the colour change around pH 4 from the red (acidic) to the blue (alkaline) form. Thymol blue has two colour changes: with increasing pH, the first colour change is around pH 2 from the red to the yellow, the second one is around pH 9 from the yellow to the blue. We have added a small amount of the indicator to the gel during preparation. The total concentration of the dye in the gel was not higher than 10^{-2} M approximately. No indicator has been present in the electrolyte inlets.

The main advantage of the congo red is its almost neglectable rinsing out of the PVA gel. This is probably caused by various weak and strong interactions of the dye with the gel, the congo red in higher concentrations can be used even as the cross-linking agent for the PVA gel [9]. Under the conditions of our experiments, congo red was well retained in the PVA gel, however, its ability to exhibit a colour change with changing pH has not been affected.

The two colour changes of the thymol blue (at pH 2 and 9 approximately) makes this dye a promising marker of steep pH gradients expected to develop in the electrolyte diode.

4.3. *Different behaviour of the electrolyte diode with an addition of the dye*

As the molecules of acid–base indicators are of ionic character, they can affect charge transport through the electrolyte diode. Their mobility in the gel is, however, significantly decreased due to (i) larger molecule comparing to other ions present in the system (H^+, OH^-, K^+ and Cl^-), (ii) spatial limitations of the gel matrix and (iii) possible interactions with polymer chains. Experimental and modelling study on the decrease of the effective diffusivity of ions in PVA hydrogel has been published recently [10]. In our experiments the addition of an acid–base indicator at higher concentrations generally increases the conductivity of the gel especially in the closed mode, nevertheless, the diode-like UI characteristics is qualitatively retained as it can be seen in Fig. 9 for the pure diode and the diode with addition of thymol blue in the PVA gel (using Device A).

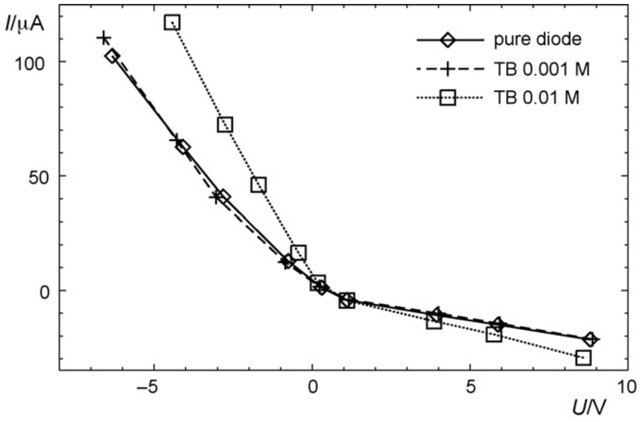

Fig. 9. The current-voltage characteristics of the electrolyte diode with addition of thymol blue (TB).

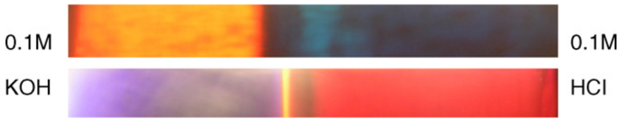

Fig. 10. Position of the acid–base boundary visualized by congo red and thymol blue (the upper and bottom image, respectively) when no external electric field is applied to the system. The images have been converted to the greyscale with enhanced contrast for printed edition, to see original colours please cf. the on-line edition.

4.4. *Experimental observations*

First set of experiments with the electrolyte diode (Device A) with acid–base indicators has been carried out without the external electric field ($U = 0$ V). Under this condition, the pH profile in the permeation layer of the electrolyte diode is similar to that in the closed mode as the acid–base boundary (the zone with significant change of pH and other variables) is rather narrow (cf. Fig. 3i, m, and r). The acid–base boundary can be found left from the center of the diode, closer to the reservoir with the alkaline electrolyte. This is caused by different mobility of H^+ and OH^- ions. Experimental results confirm this prediction: both with congo red as well as with thymol blue the colour change corresponding to the change of pH can be found left to the center of the diode closer to the inlet of the alkaline electrolyte (cf. Figs. 3i and 10).

When a negative potential difference is applied, i.e., the diode works in the open mode, the zone of the bright colour (corresponding to the pH between 2 and 9 in the case of thymol blue) expands according to the predictions of the model (cf. Figs. 3a, e and 11), the only difference is the disappearance of the red-coloured zone at higher voltages (−10 V in Fig. 11).

When positive potential difference is applied, i.e., when the diode goes to the closed mode, the colours change as it can be seen in Fig. 12. While in simulations of the pure diode (without addition of indicators) the position of the acid–base boundary almost does not change, in experiments (here shown for thymol blue) the bright zone (yellow in reality) corresponding to the zone between pH values 2 and 9 approximately is moving to the left and also it is broadening. The left dark field (cf. Fig. 12, bottom, blue in reality) disappears for voltages above 1.9 V.

Fig. 11. Experimental results for negative external potential difference (i.e., the diode in the open mode) for thymol blue in Agar gel. For potential difference −5 V the left dark field marks the area of pH above 9, the lighter central part (yellow in reality) denotes the area with pH value between 9 and 2 approximately, the dark right border of the image (red in reality) denotes pH below 2. When the external potential difference U has been set to −10 V, the red-coloured area disappeared. The images have been converted to the greyscale with enhanced contrast for printed edition, to see original colours please cf. the on-line edition.

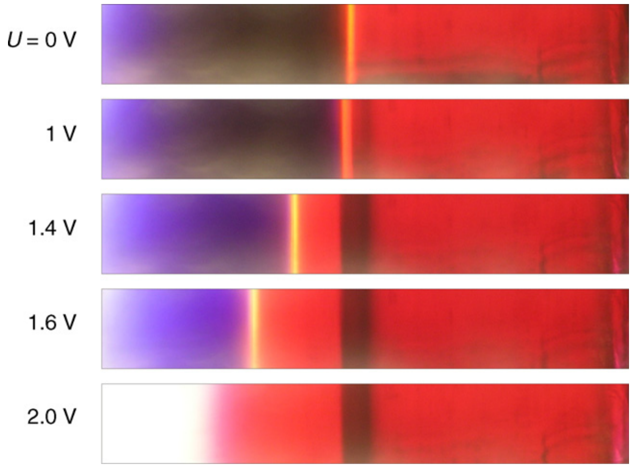

Fig. 12. Experimental results for increasing external potential difference (i.e., shifting the diode into the closed mode) for thymol blue in Agar gel. The acid–base boundary (represented by the bright strip between the two dark fields) is shifted to the left. The images have been converted to the greyscale with enhanced contrast for printed edition, to see original colours please cf. the on-line edition.

The results of the experiments with the acid–base indicator both in the closed and open mode suggest that the acid–base transient zone (between pH values 2 and 9 approximately) is shifted out of the permeation layer at higher potential differences. The explanation of this behaviour is not easy as it is a result of complex interactions of several processes. One effect which should be taken into account are the acid base equilibria of the indicator. In the case of thymol blue, up to five different forms of the indicator can be found, according to Kolthoff et al. [11]: the blue form I^{2-}, yellow or colourless forms HI^- and H_2I (two different conformations), and the red form H_3I^+ (cf. Fig. 13). When external potential difference is applied, ionic forms of the indicator migrate according to their charge. They can change their charges when entering the zone of different pH and also they can be washed out of the permeation layer when they reach the border of the permeation layer. Another effect which should be considered is possible different diffusivity of different ionic forms in the permeation layer, as well as possible interactions of the ionic forms with the gel (e.g., with ionic groups of the opposite charge fixed in the gel structure).

At low external potential differences (in absolute values, up to 1 V in the closed mode and up to 5 V in the open mode) the correspondence of the experimental results with the model predictions is quite good.

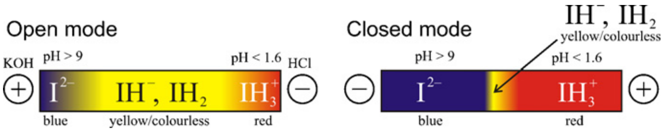

Fig. 13. Ionic forms of the thymol blue in the permeation layer. The images have been converted to the greyscale with enhanced contrast for printed edition, to see original colours please cf. the on-line edition.

5. Conclusions

We have verified experimentally the existence of steep electric potential and concentration gradients of ionic components around the acid–base boundary in the electrolyte diode. One of the methods used involved the addition of an acid–base indicator into the system. The ionic nature of indicator molecules can affect the behaviour of the electrolyte diode. At low potential differences, formation of a narrow zone with a distinctive change of pH has been observed in the closed mode, in the open mode the acid–base zone broadens as predicted by the mathematical model. At higher values of the external potential difference, the behaviour of the electrolyte diode differs from the predictions of the model (describing the “pure” diode without an acid–base indicator): experiments have shown the movement of the transient acid–base zone to the border or out of the permeation layer. This behaviour is probably caused (i) by participation of indicator particles in charge transport in the permeation layer (the isoelectric focusing can be one of the effects), (ii) by acid–base equilibria of different ionic forms of the indicator, as well as (iii) by interaction of the indicator particles with the gel matrix. The detailed explanation of the influence of the indicator would require additional experimental and modelling studies. We are working on the extension of our recently published [4] non-equilibrium model of the electrolyte diode with mass balances and acid–base equilibria of ionic forms of the acid–base indicator.

Another experimental technique used was the measurement of the electric potential profile in the electrolyte diode. The steep potential change around the acid–base boundary located near the alkaline electrolyte reservoir has been found as predicted in the results of mathematical modelling. The significant advantage of this measurement is the possibility to measure the potential profiles also with higher external voltages (we have successfully tested the external voltages up to 20 V; even higher voltages are possible to use, the problem is formation of bubbles on the working electrodes especially in the open mode, where the current passing through the permeation layer is significantly higher).

The earlier works concentrated on the measurement of overall current-voltage curves. We are trying to explain the behaviour of the systems with more detailed approach, as the advanced microtechnology methods allow us to study the system by direct methods inside. The electrolyte diode is an example of relatively simple microsystem with steep spatial gradients. The methodics developed here can be used for studies of similar microfluidic systems using the external electric field.

In the next work we plan further decrease of dimensions of the electrolyte diode and its integration into a more complex microfluidic device as a functional part.

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