

Electrolyte diodes and hydrogels: Determination of concentration and pK value of fixed acidic groups in a weakly charged hydrogel

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Current-voltage (CV) characteristics of polyvinyl alcohol (PVA) - glutaraldehyde hydrogel cylinders were measured in aqueous KCl solutions. To this end a new special apparatus was constructed where the gel cylinder connects two electrolyte reservoirs. The measured quantities are the electric current flowing through the gel and the potential difference between the two reservoirs. Concentration polarization near the gel-liquid interfaces is decreased considerably by applying an intense mechanical stirring in both reservoirs. Under these conditions below 1 V concentration polarization is negligible, and the CV curves are nearly straight lines. It was found that the gel applied here is a weakly charged anionic hydrogel. Concentration of fixed anions was determined from the slope of these lines measured in 0.001 and 0.01 molar KCl solutions. Fixed anion concentration of the same piece of gel was measured also with a different method, when the gel was used in an acid-base diode. In this case one reservoir contained 0.1 molar HCl, and the other 0.1 molar KOH. From the results of the two measurements, the concentration (4.45×10^{-3} M) and the pK value (4.03) of the fixed acid groups responsible for the anionic character of the gel was calculated. The pK value is compatible with fixed carboxylic acid groups contaminating the PVA gel. Furthermore, concentration polarization phenomena in the boundary layers nearby the gel were studied in 0.001 M KCl solutions, measuring the diodelike CV characteristic of a gel cylinder, when stirring was applied only at one side of the gel. Boundary layers facing the cathode or the anode responded in a different way to stirring. The difference cannot be explained completely with the hypothesis of electroconvection suggested previously.

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I. INTRODUCTION

A. Background of the research

Nonlinear chemistry [1–4], engineered complexity [5], biological analogies, and possible analytical applications [6] motivated the research initiated in the past few years in the field of the electrolyte diodes and transistors [3,4,6–10]. The "building block" of these devices is a hydrogel cylinder connecting reservoirs of two different electrolytes. In most cases one reservoir contains an aqueous solution of a strong acid (e.g., 0.1 M HCl), while the other contains a strong base (e.g., 0.1 M KOH). The material of the cylinder is polyvinyl alcohol (PVA) crosslinked with glutaraldehyde, as this hydrophilic polymer network in an aqueous medium forms a hydrogel which is stable enough both in acidic and in alkaline solutions. Acid-base reactions, ionic diffusion and migration take place in the gel nearly like in a free aqueous solution, but the polymer network practically eliminates any possibility for a mixing of the reaction components by convection. Gels are often applied in reaction-diffusion experiments to suppress convection [11–13]. An advantage of the PVA based gels compared to other hydrogels is that the concentration of fixed charges (fixed ionizable groups) is very low. The effect of these fixed charges of the PVA can be

neglected in most gel experiments [14]. We found, however, that in the case of electrolyte diodes and transistors even a low concentration of fixed charges can affect considerably their current-voltage (CV) characteristics.

In a recent paper [8] we made an attempt to determine the concentration and the chemical nature of the ionizable groups of the PVA gels. To eliminate any reactions of the acidic or alkaline solutions with the gel matrix we studied the CV characteristics of PVA based gel cylinders in various KCl solutions. Electric current flowing through the cylinder connecting two identical KCl solutions was measured as a function of the voltage drop on the cylinder. To sustain constant KCl concentrations at both ends of the cylinder steady flows of KCl solutions were maintained during the experiment by a peristaltic pump. In our previous work [8] we recorded CV characteristics, which were strongly non-linear due to concentration polarization in the boundary layers of the gel. While this proved the presence of fixed negative charges in the gel qualitatively, at the same time it prevented quantitative measurements, as the exact thickness of the boundary layers was unknown. Consequently, we could only estimate that the fixed charge concentration was around 10^{-3} M. In those experiments polarization phenomena in the boundary layers were dominating, because those layers were relatively thick, as the flow of the peristaltic pump did not provide enough stirring at the gel-liquid interface.

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B. Aims of the present paper

The first aim of the present work is to perform gel polarization experiments with an intense mechanical stirring applied at both ends of a gel cylinder to reduce the thickness of the boundary layers, and this way to obtain CV curves from which a quantitative determination of the fixed charge concentration is possible.

Second, we want to perform acid-base diode experiments on the same gel cylinder, where the gel connects 0.1 molar HCl and 0.1 molar KOH solutions. This system behaves like a diode [6] because at positive polarities the gel is filled with conductive KCl solution whereas at negative polarities a high impedance region of pure water appears. From the CV characteristics of such a diode the fixed charge density can be also calculated [6], but with a different method and at a different *pH*. Based on these data the *pK* value of the acidic group fixed on the polymer chain can be determined. The result can be compared with *pK* values of various carboxylic acids including those where the carboxylic group is attached to a PVA chain [15].

It was an element of uncertainty, however, that the calculation of the fixed anion concentration from acid-base diode experiments applied an approximate analytical formula only. Thus it was also an aim of the present work to compare these results with numerical simulations avoiding these approximations. It is shown here that diode currents, concentration profiles and fixed charge densities calculated by the analytical formulas and by numerical simulations agree within 5% or better.

Finally, we want to study the effect of stirring on the anodic and on the cathodic boundary layer separately. When only one KCl reservoir is stirred and the other one is not, a diodelike CV characteristic can be expected due to that asymmetry. Moreover this way we can check whether electroconvection really occurs in the anodic boundary layer of the gel. This hypothesis was introduced in our previous paper [8] (based on analogous phenomena in ion exchange membrane studies [16]) to explain the lower than expected concentration polarization in the anodic boundary layer.

C. Perspectives of the research

This paper is a part of a research program devoted to the study of polarization phenomena nearby and inside weakly charged hydrogels. These studies are focused on situations which yield an asymmetric CV characteristic that is when a diodelike behavior can be observed. We regard three possible sources of such an asymmetry: (i) asymmetric stirring (discussed here beside the method of the fixed charge determination, which is the main topic of the present paper), (ii) asymmetric concentrations at the boundaries, and (iii) asymmetric fixed charge distribution inside the gel.

In these experiments gel polarization phenomena are studied independently from the electrochemical processes of the electrodes, as in our apparatus the electrodes are not contacting the gel directly but placed far away from it and consequently have no influence on the results. The main aim of these studies is to learn more about the polarization phenomena at liquid-weakly charged gel interfaces, which can ex-

hibit peculiar phenomena [17] and play an important role in biological systems [18,19]. Biological gels are usually weakly charged, and their fixed groups are also weak acids or bases.

II. EXPERIMENTAL SECTION

A. The gel

Chemicals. Polyvinyl alcohol (nominal molecular weight 15000, degree of polymerization 300, degree of hydrolyzation: 89%, Fluka), glutardialdehyde (25% aqueous solution, Reanal) were used without further purification. All other chemicals were of reagent grade.

Gel recipe. 2.5 g polyvinyl alcohol solution (30% w/w) was prepared with distilled water, which was degassed to prevent bubble formation in the later steps of the procedure. 0.5 mL glutardialdehyde solution (2% w/w) and 0.5 mL distilled water were added to the PVA solution, and the mixture was homogenized by stirring with a glass rod (gently, to avoid bubble formation). Finally, 0.25 mL 5 M HCl was added under continuous stirring. As the gelling of this mixture is rather fast (the mixture can be handled as a liquid for 3 minutes at room temperature), it was used immediately to prepare gel cylinders.

Preparation of gel cylinders. The freshly prepared liquid mixture was poured into the open cylinder of a 5 mL plastic syringe, from which the piston was removed. Then the piston was reinserted, and, by pressing the piston, the viscous mixture was forced to fill a silicon tubing (inner diameter 1.2 mm, outer diameter 2 mm) attached to the syringe. After 2–3 hours the silicon tubing containing the hardened gel was placed into hexane to swell. The swelling was facilitated with a gentle stirring for 1–2 minutes. The thin gel cord was removed from the swollen tubing by pumping hexane through it. The free cord was washed with distilled water. For later use it was cut up into approximately 50–60 mm long pieces, which were stored in distilled water at 5 °C in the dark, to avoid algae growth.

Inserting the gel cylinder into a sample holder. Prior to the measurements the gel samples studied in our experiments were inserted into sample holder PVC disks. Such discs served as the wall, separating the anodic and cathodic sides, when installed into the apparatus (see Fig. 1). The 3.2 mm thick PVC disks had a central bore with 0.7 mm nominal diameter to accommodate the gel. Before placing the gel cylinder into the sample holder the gel had to be shrunk, as its wet diameter was larger than that of the bore. This was achieved by drying the gel cord overnight, at room temperature in the laboratory atmosphere, in a rectangular PTFE (“teflon”) channel. (The channel prevented strong bending of the gel while it was shrinking. The bending is due to a mechanical instability caused by the drying.) The dry gel cord was cut up into 4–5 mm long small cylinders. A dry and hard gel cylinder was pushed into the hole of the disk. In the next step the PVC disc with the gel cylinder was placed into distilled water, where swelling of the gel closed completely the hole as a “plug.” After this procedure the PVC disks with the gel samples were stored under distilled water at laboratory temperature in the dark at least for 10 days before measure-

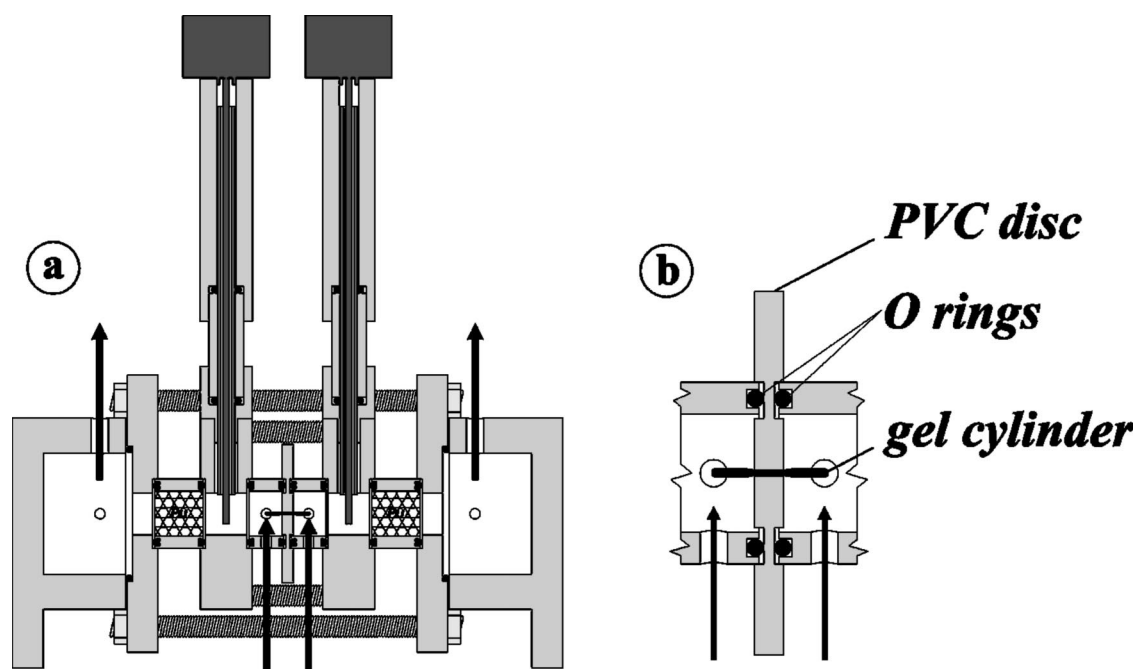


FIG. 1. (a) Cross-sectional view of the Plexiglas apparatus. Arrows indicate the continuous flow of electrolytes. Voltage sensing electrodes are outside of the apparatus, but connected electrically with the small cylindrical reservoirs on the two sides of the PVC disk by electrolyte channels to measure the potential drop on the gel cylinder (circles indicate their joining points). Current electrodes are mounted into the outer larger reservoirs (circles show their position). PU: polyurethane foam. DC motors driving the stirrers are placed on the top of the two plexiglas tubes. (b) Enlarged view of the PVC disk with the gel cylinder.

ments, because the swelling in the narrow bore is a slow process. Using wider bores could shorten this time, but in that case the gel cylinder creeps out of the hole at high voltages [8].

B. Apparatus

The apparatus is depicted in Fig. 1. The PVC disk with the gel is displayed Fig. 1(b). Flows of the fresh electrolytes enter at the bottom of the apparatus, close to the gel on both sides.

Compared to the previous experimental setup [8], the apparatus has been modified, by adding a stirrer on both sides of the gel. The stirrers were made of PTFE tubing (outer diameter: 1.7 mm, inner diameter: 0.9 mm). They were attached to the shafts of the driving DC motors. Each tubing was spinning in a bore (diameter: 3 mm) except their last 8–10 mm, where the movement of the tubing was not limited. This way the ends of the flexible PTFE tubing could move freely in the solution, providing a strong stirring effect. The stirring was vigorous enough to break up bubbles that we have injected for the inspection of the stirring. The path of the resulting small bubbles showed an intense mixing of the fluid. While the flow was intense and turbulent, it was far from making any damage to the gel cylinder (like causing cracks in or breaking pieces off the gel). For symmetry reasons on both sides of the gel identical motors, tubing and stirring speeds were applied, unless otherwise stated.

From the stirred compartment the electrolyte flows to a large reservoir across a porous plug made of polyurethane foam. The continuous flow and the porous plug prevents that

any products of the electrolysis generated at the current electrodes contaminate the fresh electrolyte around the gel cylinder.

C. Electrodes

Ag/AgCl voltage sensing electrodes were applied. No extra salt bridge was necessary in the case of KCl solutions: the electrodes were placed into the feedstreams directly. A combined salt bridge, consisting of 10 M NH_4NO_3 and 1 M KCl solutions, was used in the acid-base diode experiments, when the electrolytes were 0.1 M KOH and 0.1 M HCl in the left and right side of the apparatus, respectively. The high concentration of ammonium nitrate was necessary to minimize liquid junction potentials. The Ag/AgCl electrodes were immersed into the 1 M KCl solution. The current electrodes were made of platinum wire.

D. Calibration of the measuring cell. Calculation of the parasitic potential drops

As a first step the apparatus was calibrated: CV characteristics were measured first with 0.001 M and then with 0.01 M KCl solutions, but without the gel. This procedure was necessary to determine the parasitic (but inevitable) ohmic potential drops between a voltage sensing electrode and the nearby mouth of the capillary, where the polarized part of the gel cylinder starts. To obtain the actual voltage on the gel cylinder, the measured voltage has to be corrected by subtracting these unwanted potential drops. The overall (or total) resistance between the voltage sensing electrodes can be eas-

ily obtained from the measured voltage U_M and current I , as $R_T = U_M/I$. That overall resistance is a sum of three resistors connected in series: two symmetric resistors representing the electrolyte connection between the electrodes and the capillary mouths, and the third is the capillary itself. When the apparatus is filled with a homogeneous electrolyte solution with a uniform specific resistance, then the potential distribution in the measuring cell and the ratio of the resistances can be calculated from the geometry of the measuring cell, without knowing the actual value of the specific resistance. The result of a numerical simulation of the potential distribution using the FEMLAB® program [20] is shown in Figs. 2(a) and 2(b).

The relative resistance (the resistance compared to the total resistance) of a finite element between two equipotential surfaces can be calculated as a ratio of the potential difference on that finite element, compared to the overall potential difference. The capillary has not a “flat” but a “rounded” end, as the equipotential surfaces are curved at its mouths [see Fig. 2(b)]. For such a round ended capillary an equivalent length can be calculated: it is the length of a flat ended capillary which would have the same resistance. The result is 3.3 (3.29) mm, i.e., a 0.1 mm increase that is due to the rounded end, which means a mere 0.05 mm correction at each ends.

When the capillary is filled with a gel, which is a medium of different conductivity, the potential distribution and the shape of the equipotential surfaces around the capillary mouth are modified a little, as Fig. 2(c) shows. The equivalent length of the capillary is somewhat larger now: it is 3.32 mm. Nevertheless, these corrections are well within the experimental error. Numerical simulations show, however, that the value of the resistance between a voltage electrode and the nearby capillary mouth can be affected somewhat, due to that part of the gel which is not inside the capillary, if the specific resistance of the gel is higher than that of the surrounding electrolyte. That increase can be calculated from the measured total resistance, as it is shown in Appendix A. In the last step the actual values of the three electrolyte resistors were determined from the measured overall resistance and from the calculated relative ones. The parasitic resistances applied in our calculations are summarized in Table I. As can be seen, when a gel is placed into the capillary the parasitic resistances are increased somewhat (see Appendix A for details). Using the values of Table I, and the actual current flowing through the cell in a given measurement, the parasitic potential drop was eliminated from the measured voltage to obtain the actual (or net) voltage on the measuring capillary filled with the electrolyte or the hydrogel cylinder. All measured voltages were corrected this way, i.e., the diagrams in the paper display the net voltages only. The corrections were always less than 20% of the measured voltage, typically around 10%.

E. Measuring the CV curves of the gel cylinders. Relaxation times and the geometry of the capillary

After the complete swelling of the gel the measurement of a CV curve was still not a fast procedure: to reach a steady

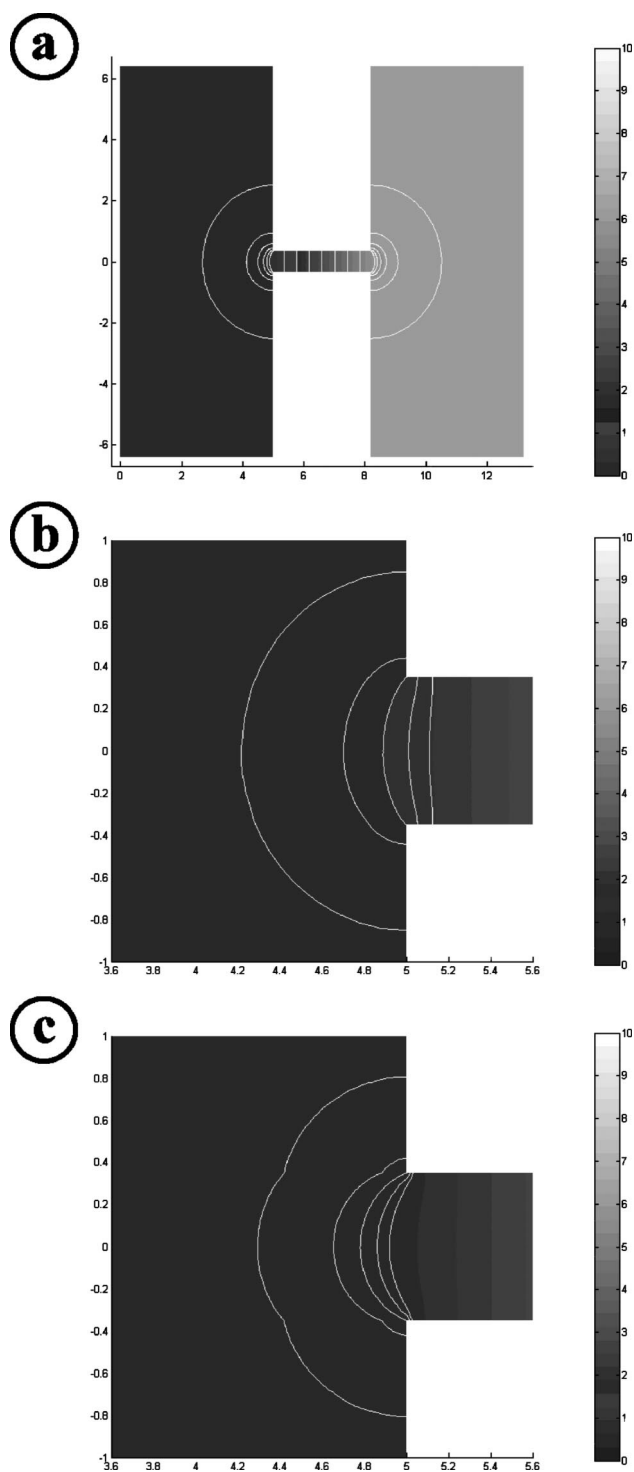


FIG. 2. Calculated equipotential surfaces (cross-sectional view) (a) in the measuring cell, (b) and (c) around the mouth of the capillary. (a) and (b): The cell is filled with a homogeneous solution: the specific resistance is uniform. (c) The capillary is filled with a long gel whose specific resistance is 4 times larger than that of the surrounding solution. The gel cylinder sticks out from the capillary, its outer part is 5 mm long at both ends. Geometrical data are given in mm. The grey scale represents potential between 0 and 10 V. The difference between the equipotential surfaces is (a) 1.1 V within, and 0.11 V outside the capillary, (b) uniformly 0.22 V, and (c) uniformly 0.08 V.

TABLE I. Parasitic resistance as a function of the experimental conditions.

KCl concentration	Electrolyte in the capillary	Gel in the capillary
0.001 M	78.1 k Ω	88.6 k Ω
0.01 M	8.28 k Ω	10.3 k Ω

state current within the experimental error (when any unidirectional drift ceased at a fixed voltage) required 1–2 hours. This is because the diffusion time constant τ ($\tau=L^2/\pi^2D$) of an open ended capillary is about 1000 s, assuming that the diffusion coefficient D is 10^{-5} cm²/s. The time to obtain a steady state value for a given point of the CV diagram could be reduced substantially (to less than one hour), if the measurement was started with the most positive or with the most negative voltage and was gradually decreased to zero. When applying this procedure to obtain the first point with the highest voltage still required 2–3 hours, but the other steady states were reached much faster.

These time consuming procedures could have been greatly accelerated by reducing the active length of the capillary, i.e., by decreasing the thickness of the PVC wall separating the electrolyte reservoirs. From a purely technical point of view an order of magnitude reduction in the length (causing a decrease in the diffusive relaxation times by two orders of magnitude) would be quite possible, as a 0.3 mm thick PVC wall is still strong enough. On the other hand, the aspect ratio (the length/diameter ratio, in the present experiments it is 3.2:0.7) of the capillary would be also reduced, if the diameter of the gel cylinder remained the same. At lower aspect ratios the relative resistance of the polarized part of the capillary compared to the resistance of the whole apparatus would be too small, and uncertainties concerning the region around the capillary mouth would also play a more important role. To avoid this, a simultaneous reduction of the gel diameter would be also necessary. Such a reduction, however, is not yet possible with our present technique of producing the gel cylinders.

III. RESULTS AND DISCUSSION

A. CV characteristics of the PVA gel cylinder and the gel-holder capillary in different KCl solutions

The current-voltage characteristics of a gel are shown in Fig. 3 together with that of the empty bore. Regarding that the conductivity of a 0.01 M KCl solution at 25 °C is 1.41 mS/cm [22] the Ohmic resistance of a 3.2 mm long capillary with a diameter of 0.7 mm should be 58.8 k Ω when it is filled with the above solution (or 60.7 k Ω if the effective length of the capillary is 3.3 mm). The measured value is somewhat less: it is 58.4 k Ω [see Fig. 3(b)]. The origin of that small deviation could be a 1 °C warmer temperature or a 0.01 mm wider capillary (0.70 mm was only the nominal diameter of the drill.) That small uncertainty in the absolute value, however, will not affect our results, especially because not the absolute, but only the relative conductivity data matter in the evaluation of the measurements. For example, such

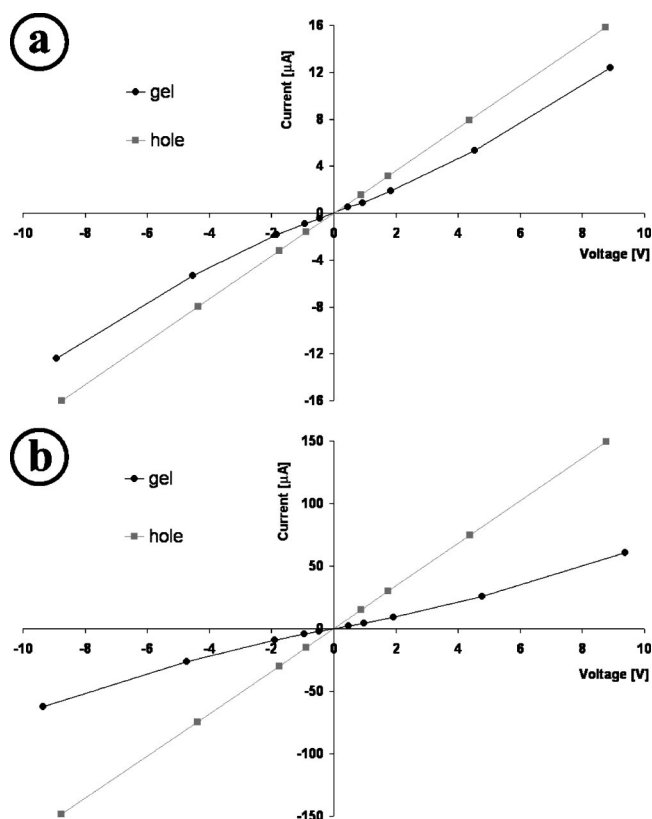


FIG. 3. Steady state CV characteristics of the gel cylinder (circles). KCl concentration in the outer electrolyte: 0.001 M (a) and 0.01 M (b). Both figures display the CV characteristics of the bore as well (when there is no gel but only the outer electrolyte flowing mildly through the capillary [21]) for comparison (squares).

a relative value is the ratio of the conductivities measured with the same capillary filled with 0.01 M and 0.001 M KCl solutions, respectively. The theoretical value of that ratio is 9.6, as can be calculated from conductivity data [22]. The measured value in Fig. 3 is 9.4. The small deviation is due to the greater than theoretical conductivity of the 0.001 M solution, caused by some dissolved carbon dioxide. (CO₂ was absorbed from the laboratory atmosphere during the preparation of the solutions). The increase of the conductivity caused by the same CO₂ level is relatively smaller in a 0.01 M KCl solution. What really matters is the conductivity (or resistance) ratio of the gel in the two different electrolyte solutions. The resistance of the gel (in the linear -1 V, $+1$ V region) is 996 k Ω in 0.001 M KCl and 234 k Ω in 0.01 M KCl. Thus the conductivity is increased by a factor of 4.26 ± 0.1 . (The experimental error is mainly due to slight changes in the laboratory temperature between two measurements. Care was taken that this was never more than ± 1 °C.)

B. Calculation of the fixed charge concentration from the measured CV curves

As Fig. 3 shows the CV curve can be approximated with a straight line at relatively small voltages (in Fig. 3 between -1 V and $+1$ V). Within this range concentration polarization phenomena are negligible and the ion concentrations

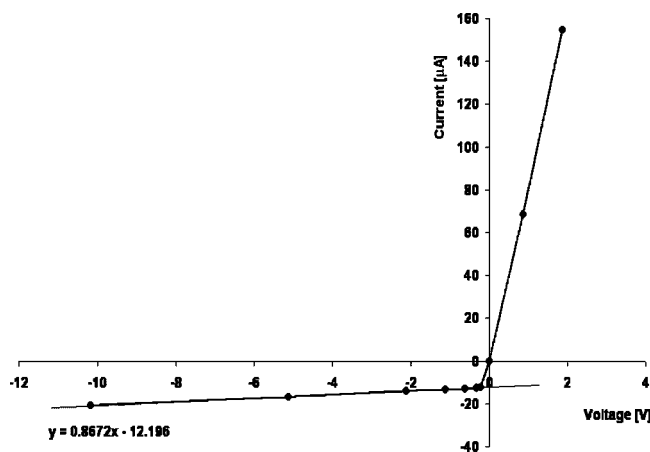


FIG. 4. Current-voltage characteristics of the gel cylinder of Fig. 3 when it is working as an acid-base electrolyte diode. Here the cylinder connects 0.1 M KOH and 0.1 M HCl solutions.

inside the gel can be regarded as uniform. The conductivity and the fixed ion concentration of the gel can be calculated from this linear part of the CV curves. The conductivity of the gel is due to its mobile ions, whose concentration is determined partly by the outer electrolyte and partly by the fixed ions inside the gel. Thus gel conductivities measured with various outer electrolyte concentrations can give information about the fixed charge concentration of the gel. In Appendix B a formula is derived (based on the Donnan equilibrium and electroneutrality condition), according to which the ratio α of the gel conductivities measured in two different KCl solutions (concentrations c_{01} and c_{02}) can be expressed as

$$\alpha = \frac{\sqrt{1 + \left(\frac{2c_{02}}{a_F}\right)^2} - 0.02}{\sqrt{1 + \left(\frac{2c_{01}}{a_F}\right)^2} - 0.02},$$

where a_F is the concentration of the fixed anions. Knowing α from measurements (here it is 4.26 ± 0.1 determined from Fig. 3) the above formula was used to calculate the fixed charge concentration, yielding $a_F = 4.45 \pm 0.15 \times 10^{-3}$ M.

C. Calculation of the fixed charge concentration from the acid-base diode characteristics

Another method to determine the fixed charge concentration in the gel is to measure its CV characteristics in an acid-base diode [6]. To this end the very same gel cylinder was applied, but now the two reservoirs contained 0.1 M KOH and 0.1 M HCl solutions connected via the hydrogel cylinder. Stirring was also applied in these experiments but it had minimal or no role now, as the resistance of the alkaline and the acidic solution was always negligible compared to that of the gel cylinder. This was especially true for the reverse biased diode, which was the important case here. CV characteristic of a diode is shown in Fig. 4. In the forward direction K^+ ions from the alkaline reservoir and Cl^- ions from the acidic reservoir migrate into the gel under the influence of the applied electric field and form a well conducting KCl solution there. Thus the positive branch of the CV

characteristic is similar to that when both reservoirs contain 0.1 M KCl solution: the current increases linearly with the voltage. In the reverse biased diode the situation is different: now the hydroxyl and hydrogen ions migrate into the gel cylinder where they recombine. As a result a thin layer of pure water is formed whose conductivity is very low. Thus, in the absence of fixed ions, theory predicts a small and nearly voltage independent (practically constant) current for the negative branch of the CV diagram. However, if fixed anions can be found in the gel, then a current component increasing with the voltage also appears in addition to the constant component. It was realized that the slope of the CV diagram is proportional to the concentration of the fixed ions in this case. (The conductivity increase is due to the mobile counterions contaminating the otherwise high resistance zone of pure water. Now the electric field is not able to remove all the mobile ions from that zone as the electroneutrality condition would be violated if the fixed ions would remain alone.) It was shown [6] that the concentration of the fixed anions a_F can be calculated from s_R , which is the slope/intercept ratio of the negative branch, according to the following formula:

$$a_F = 2 \left(1 + \frac{D_{OH}}{D_H} \right) c_0 s_R,$$

where c_0 is now the concentration either of the acid or the base (0.1 M in the present case), D_{OH} and D_H are the diffusion coefficients of hydroxyl and hydrogen ions. Applying the above formula and the data of Fig. 4, the fixed anion concentration was found to be 5.7×10^{-4} M; see note [23]. The 5.7×10^{-4} M fixed charge concentration obtained by the acid-base diode method is nearly one order of magnitude smaller than the 4.45×10^{-3} M value, which was calculated earlier from CV characteristics measured in KCl solutions.

D. The cause of the deviation in the fixed charge concentration measured with the two methods. Calculation of the pK value of the ionizable groups of the gel

The deviation can be explained with the different pH values in the two experiments, and can be applied to determine the pK value of the weak carboxylic acid, which provides the fixed ionizable groups in the gel. To this end we can assume that in the KCl solution practically all fixed acidic groups are dissociated, thus the concentration of the fixed anions is approximately equal to the total concentration of the fixed groups. This is because the pH of the KCl solution is between 5.6 and 6 (due to some dissolved CO_2), and at this pH an acid with a pK value around 4 (calculations supporting this value will be presented later) is mostly dissociated. This can be proven regarding the following relationship:

$$K_d = \frac{c_H a_{F1}}{c_{HA1}} \Rightarrow \log \left(\frac{c_{HA1}}{a_{F1}} \right) = pK - pH.$$

Here K_d is the dissociation constant of the weak acid, a_{F1} is the concentration of the fixed anions in the gel when it is in a KCl solution, and c_{HA1} is the concentration of the nondissociated carboxylic groups. It can be seen that the c_{HA1}/a_1

ratio is between 0.01 and 0.03, depending on the pH . Consequently, it is justified to assume that

$$c_T \approx a_{F1},$$

where

$$c_T = c_{HA} + a_F,$$

that is c_T is the sum of the dissociated and non-dissociated carboxyl group concentrations which is an invariant quantity. In the acid-base diode experiments it is assumed that there are only hydrogen ions in the high impedance zone and fixed anions, whose concentration is a_{F2} now. (The hydroxyl ion concentration can be neglected in that zone.) In this case according to the electroneutrality condition

$$a_{F2} \approx c_{H2}.$$

Taking into account that c_T is independent of the degree of dissociation, we can write

$$c_{HA2} = c_T - a_{F2} \approx a_{F1} - a_{F2}.$$

Consequently,

$$K_d = \frac{c_H a_{F2}}{c_{HA2}} \Rightarrow pK = \log(a_{F1} - a_{F2}) - 2 \log(a_{F2}).$$

According to our measurements the fixed anion concentration of the PVA gel in KCl solutions is $a_{F1} = 4.45 \times 10^{-3}$ M, while in the acid base diode experiment it is only $a_{F2} = 5.7 \times 10^{-4}$ M. Thus the pK value of the fixed acidic groups in the gel is 4.08 applying the above formula for K_d . This value is rather close to the 4 found experimentally [15] as an average pK value for carboxylic acid groups at the end of PVA chains. Consequently, this result supports strongly the conjecture that the fixed anions in the PVA gel are dissociated carboxylic acid groups.

The presence of these groups can be explained in the following way. PVA is produced from polyvinyl acetate (PVAc) via hydrolysis, and PVAc is made by polymerizing the vinyl acetate monomer. It is known [24] that chain transfer to monomer is important during the polymerization. This reaction results in an unsaturated endgroup, and hydrolysis of that gives a carboxylic acid endgroup. Thus it is reasonable to assume that the fixed ionic groups in our experiments are ionized carboxylic acid endgroups of the PVA.

The above results can be affected slightly by (i) the swelling of the gel and (ii) the accuracy of the applied analytical formula.

Swelling of the gel in the alkaline part of the acid-base diode could modify somewhat its CV characteristics as the mobility of the ions increases and the concentration of the fixed groups decreases with swelling. These two effects, however, should be minor in the neutral zone of an acid-base diode, moreover their influence on the conductance is opposite, thus the slope/intercept ratio of the negative branch will not be affected significantly.

The accuracy test of the analytical formula is discussed in the next paragraph separately.

E. Comparison of the results obtained by formulas based on analytical approximations with the results of numerical calculations

The evaluation of the acid-base diode experiment was based on an approximate analytical solution of the problem and the calculation of the fixed charge concentration utilized 3 major simplifications: (i) electroneutrality was supposed rather than applying the Poisson equation, (ii) acid-base equilibrium was assumed instead of calculating with the rate of the hydrogen ion–hydroxyl ion reaction and (iii) most importantly the gel was divided into three zones assuming linear concentration profiles within the zones [an acidic zone in the left, a weakly acidic in the middle, and an alkaline zone in the right part of the diode; see Fig. 5(a)].

To check the validity of these approximations we performed numerical simulations with the IonLab program [25] based on the exact equations without the above simplifications. The results of the simulations are shown in Fig. 5(b). The basis of the approximate analytical calculation is that while the electric current density i should be the same in all the three regions there is a unique expression for i in each region [6]:

$$\frac{i}{F} = \frac{2D_H c_0}{\Delta x_H} = \frac{2D_{OH} c_0}{\Delta x_{OH}} = \frac{D_H a_F \Delta \varphi}{\Delta x_{WA}},$$

where the length of the acidic region Δx_H plus the length of the weakly acidic and the alkaline regions (Δx_{WA} and Δx_{OH} , respectively) gives the total length (here: 1 mm) of the one dimensional acid-base diode. (Here $D_H = 9.31 \times 10^{-5}$ cm²/s, $D_{OH} = 5.26 \times 10^{-5}$ cm²/s the diffusion coefficients of the hydrogen and hydroxide ions [26,27], respectively, $c_0 = 0.1$ M, $\Delta \varphi$ is the dimensionless voltage, $\Delta \varphi = \Delta U F / RT$, and F is the Faraday number.) It can be seen that the results of the analytical approximation are rather close to that of the numerical simulations. For example, the length of the zones agree rather well:

$$\Delta x_H (\mu\text{m}): 471 \text{ (anal. approx.)}, 488 \text{ (numerical)},$$

$$\Delta x_{WA} (\mu\text{m}): 262 \text{ (anal. approx.)}, 258 \text{ (numerical)},$$

$$\Delta x_{OH} (\mu\text{m}): 267 \text{ (anal. approx.)}, 254 \text{ (numerical)}.$$

The small deviation is mainly due to a very narrow recombination zone between the weakly acidic and alkaline regions, which is not taken into account in the analytical approximation. Comparing the slope and the intercept of the CV characteristics of the reverse biased diode:

$$\text{slope } (\mu\text{A V}^{-1} \text{ mm}^{-2}): 19.94 \text{ (anal. appr.)}, 19.96 \text{ (num.)},$$

$$\text{intercept } (\mu\text{A mm}^{-2}): 281.5 \text{ (anal. appr.)}, 267.1 \text{ (num.)}.$$

As can be seen the slope agrees well but the approximate intercept is about 5% higher than the more exact numerical value. (Again, the main reason of this small deviation is that the analytical approximation neglects the recombination zone.) This way the concentration of the fixed anions in the middle region of the acid-base diode (which was calculated from the slope per intercept ratio) was underestimated also

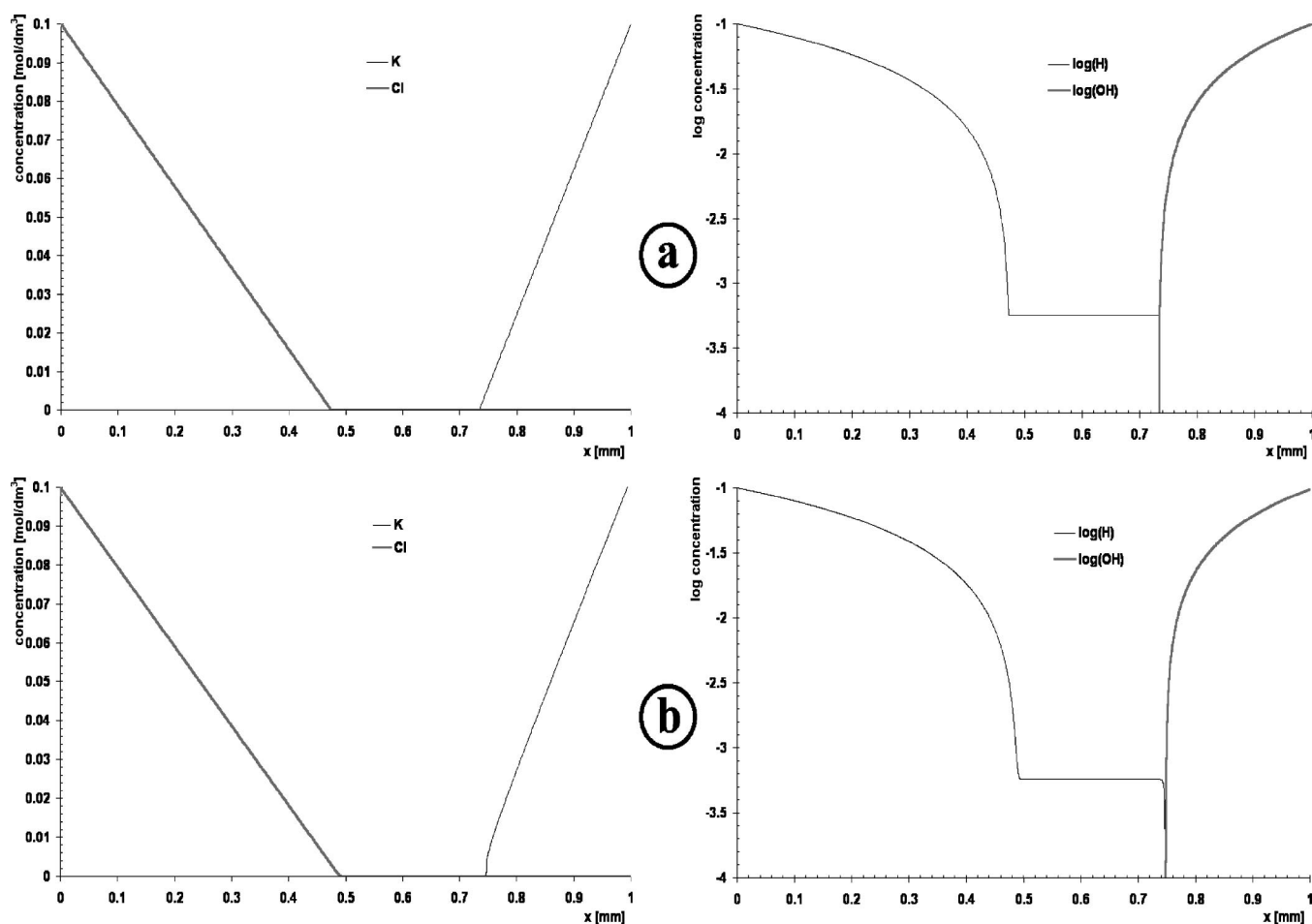


FIG. 5. Calculated concentration profiles in a reverse biased ($U=-5V$) 1 mm long acid-base diode containing fixed ionizable acidic groups $c_T=4.45 \times 10^{-3}$ M; $pK=4.08$. (a) Analytical approximation; (b) numerical simulation. 0.1 M HCl is applied at the left-hand side ($x=0$) and 0.1 M KOH at the right-hand side ($x=1$).

by 5%. Applying this correction modifies the calculated pK value from 4.08 to 4.03, thus it gets even closer to the expected value of $pK=4.0$.

Figure 5 shows that the analytical approximation is also satisfactory regarding the concentration profiles inside of an acid-base diode with fixed ionizable groups: the profiles in Fig. 5(a) (analytical formula) and Fig. 5(b) (numerical solution) are very close to each other.

F. An electrolyte diode with asymmetrically stirred boundary layers. The effect of stirring on the anodic and cathodic boundary layer

The CV characteristics of the gel in KCl solutions as displayed in Fig. 3 were recorded when both electrolyte reservoirs were stirred vigorously. Due to the violent stirring the CV curves are linear within the experimental error in the $(-1V, +1V)$ interval, which proves that concentration polarization effects are practically eliminated in this voltage region. At higher voltages, however, (especially above $+5V$ or below $-5V$) a clear departure from the linear response can be observed. This indicates the presence of some concentration polarization phenomena. It is generally accepted that these phenomena are originated in the stagnant boundary layers

adjacent to the gel. As there are fixed negative ions in the gel the transport number of the potassium ion is higher there than that of the chloride ion. On the other hand, in the free liquid the two transport numbers are nearly equal. The concentration polarization is caused by this jump in the transport numbers at the gel-solution interface, when a polarizing current is applied. In the cathodic boundary layer (the boundary layer facing to the cathode), an accumulation of the electrolyte will occur, while in the anodic boundary layer a depletion can be expected.

In case of symmetrical mechanical stirring no significant difference can be expected between the thickness of the cathodic and anodic boundary layers. In this case concentration polarization in the anodic region should determine a polarographic limit current [28]. Thus a CV curve with a decreasing slope, and approaching to a constant limit value can be expected. The experimental observation is just the opposite: the slope of the CV curve is increasing with the voltage and as a consequence no limit current can be observed. Obviously the assumption of the symmetric boundary layers is not valid: some unknown perturbing effect diminishes the thickness, and/or the impedance of the anodic boundary layer considerably. To explain this observation we suggested [8] that electroconvection [16] occurs in the anodic boundary

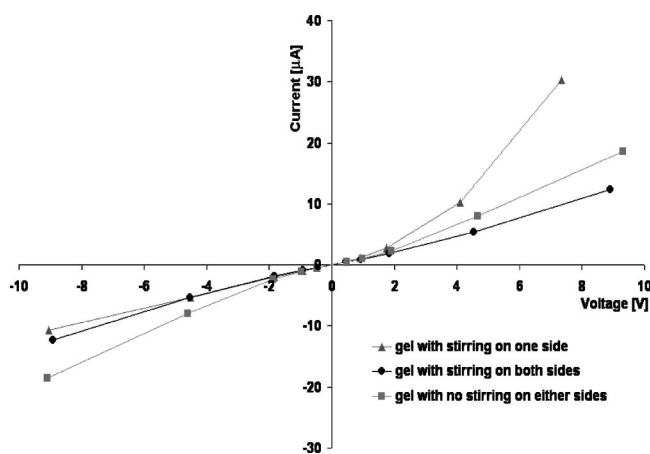


FIG. 6. Effect of asymmetric stirring on the CV characteristics of the gel. The polarity is positive when the anodic reservoir is stirred.

layer. Such a convection would be able to mix salt from the bulk to the boundary layer, reinstating the salt concentration there, at least partially. This way electroconvection could decrease the otherwise high impedance of the anodic boundary layer.

With the new apparatus introduced here an experimental test of the above electroconvection hypothesis becomes feasible. In this apparatus we could stir either one, or the other reservoir independently. This way the effect of stirring on the anodic and cathodic boundary layer can be observed separately. Figure 6 displays the result of such experiments. The CV characteristics of the gel are shown in 0.001 M KCl solution, when only one of the reservoirs is stirred. In our experiments always the same reservoir was stirred but, by changing the electric polarity the stirred reservoir could be the anodic or the cathodic one. In Fig. 6 we applied the following sign convention: the polarity is positive when the stirred reservoir is positive. For comparison, the Figure displays the CV curves when both reservoirs and when neither of them is stirred.

The CV curves recorded with symmetric stirring are odd functions: only the sign of the current depends on the polarity; its absolute value does not. On the other hand, when stirring was applied at only one side then the magnitude of the current was larger at positive polarities compared to the negative ones. Thus we have an electrolyte diode here, where the source of the asymmetry is the asymmetric stirring. The qualitative explanation of this diodelike behavior is based on the evident assumption that the boundary layer adjacent to the nonstirred reservoir should be wider than the one contacting the stirred reservoir. Thus when the polarity is positive, there is salt accumulation in the wide unstirred cathodic boundary layer. This higher concentration penetrates into the gel (that phenomenon will be discussed thoroughly in a subsequent paper) and increases its conductivity. At the same time no substantial salt depletion can occur in the well stirred anodic boundary layer. As a result the current will be considerably larger compared to the case when both sides are stirred. That can be seen in Fig. 6 where the increase can reach 100% or more. Now, at negative polarities it is the

anodic boundary layer which is unstirred. An increased width of the salt depleted zone should increase its impedance. At the same time no salt accumulation is possible now in the well stirred cathodic boundary layer. As a consequence the current should be significantly smaller than the one measured with symmetrically stirred reservoirs. In contrast to the expectations Fig. 6 shows at best a very small decrease in the measured current: it is around 10% or less even at the highest voltages, where the concentration polarization is maximum. That result is compatible with the electroconvection hypothesis: when we stir mechanically only the cathodic boundary layer the anodic side will be stirred by the assumed electroconvection thus the measured current will be similar to the case when both sides are stirred.

This way we could understand that the CV characteristic of the present asymmetrically stirred electrolyte diode should coincide at negative polarities with the CV characteristic of a gel cylinder stirred at both sides. Following the same logic we could expect that at positive polarities the diode characteristic coincides with that of a gel cylinder not stirred at either sides. But this is not the case: as Fig. 6 shows the CV characteristic measured with a gel without stirring is far from that of the diode at positive polarities. Thus the hypothesis of electroconvection ought to be refined (e.g., electroconvection provides a local mixing only limited to the immediate neighborhood of the gel but it cannot stir the whole anodic boundary layer), or other theories—like inhomogeneous fixed charge distribution in the gel—should be considered.

Theoretical and experimental analysis of these possibilities is the subject of the following papers.

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APPENDIX A: DETERMINATION OF THE PARASITIC RESISTANCE

As it was mentioned already in the main text, when a gel is placed into the capillary of our apparatus, the parasitic resistance is modified somewhat. This is because the specific resistance of the gel is higher (by a factor of 2–4 depending on the electrolyte concentration) than that of the electrolyte, and a part of the gel sticks out of the capillary increasing the parasitic resistance there. To estimate this effect we calculated CV diagrams for gels of various relative specific resistances assuming a 5 mm long piece of gel outside the capillary on both sides. (The calculations were made again with the FEMLAB program [20].) Then we constructed a diagram (see Fig. 7) where the relative parasitic resistance $R_p/R_p(\text{ref})$ was depicted as a function of the relative total resistance of the apparatus $R_T/R_T(\text{ref})$. Here $R_p(\text{ref})$ and $R_T(\text{ref})$ is the calculated parasitic and total resistance, respectively, in the reference state, that is when the apparatus is filled with a homogeneous electrolyte.

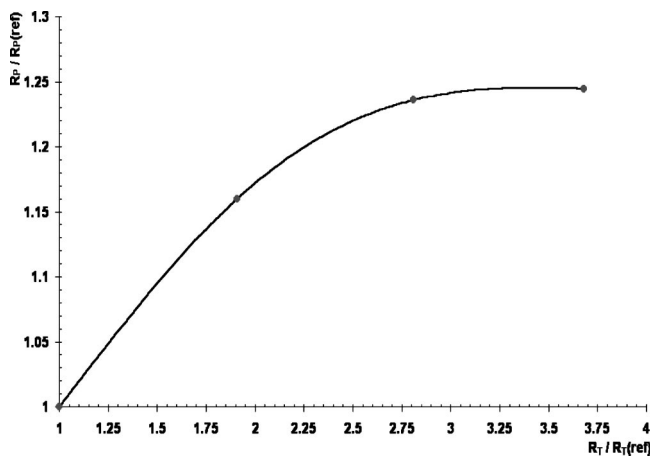


FIG. 7. The relative parasitic resistance as a function of the relative total resistance (see text for explanation).

The actual value of the parasitic resistance was determined from this diagram and from the measurements in the following way. First, $R_T(\text{ref})$ was calculated from the linear CV diagram, which can be measured when the apparatus is filled with electrolyte only. Then, using the initial linear part of the CV diagram measured with the gel, R_T was determined and $R_T/R_T(\text{ref})$ was calculated. This relative value and the diagram in Fig. 7 was applied to calculate $R_p/R_p(\text{ref})$. Finally, R_p was calculated, as $R_p(\text{ref})$ is known for 0.01 and 0.001 molar KCl solutions. The correction discussed above can increase the parasitic resistance by 20% as a maximum. Nevertheless, as the whole voltage correction due to the parasitic resistance is less than 10% of the total voltage, small uncertainties (e.g., the exact length of that part of the gel which hangs out of the capillary can deviate from the theoretical 5 mm by 1–2 mm) cannot modify our results.

APPENDIX B: DERIVATION OF THE FORMULA FOR THE CONDUCTIVITY RATIO α

Let us denote the fixed anion concentration in the gel with a_F . Then c_K and c_{Cl} —the potassium and chloride ion concentration in the gel—can be calculated taking into account the Donnan equilibrium and the electroneutrality condition. The result is

$$c_K = \frac{a_F + \sqrt{a_F^2 + 4c_0^2}}{2},$$

$$c_{Cl} = c_K - a_F,$$

where c_0 is the KCl concentration in the outer electrolyte surrounding the gel. As there is no concentration gradient in the gel the ionic currents depend only on $\Delta\phi$, the applied voltage. They can be expressed as

$$I_K = u_K c_K \Delta\phi \frac{A}{L},$$

$$I_{Cl} = -u_{Cl} c_{Cl} \Delta\phi \frac{A}{L},$$

where I_K and I_{Cl} are the molar currents of the potassium and chloride ions respectively, u_K and u_{Cl} are the ionic mobilities in the gel, A is the cross section of the gel, and L is its polarized length. The electric current is the sum of ionic currents multiplied by the molar ionic charges that is

$$I = F(I_K - I_{Cl}).$$

When we perform two experiments on the same piece of gel applying the same voltage but at two different concentrations of the outer electrolyte (here $c_{01} = 10^{-3}$ M, $c_{02} = 10^{-2}$ M), two different electric currents can be measured according to the applied concentration. The conductivity ratio α of these currents can be expressed as

$$\alpha = \frac{I_2}{I_1} = \frac{u_K c_{K2} + u_{Cl} c_{Cl2}}{u_K c_{K1} + u_{Cl} c_{Cl1}}. \quad (\text{B1})$$

It is known (as it is also illustrated by Fig. 3) that ionic mobilities in a hydrogel are smaller than in a free aqueous solution. This is because the polymer network slows down the diffusion of low molecular weight ions and molecules inside the gel. (The mobility of an ion is proportional with its diffusion coefficient which is a consequence of the Einstein relation.) As the ionic radii and the diffusion constants of the potassium and chloride ions in water are very close to each other, it is a good approximation to assume that these ions are “slowed down” by the polymer network in the same proportion [29–31]. Thus in the following we will assume that the ratio r of the diffusion coefficients of the potassium and chloride ions is independent of the medium and it is the same in free aqueous solution and in the hydrogel:

$$r = \frac{D_K}{D_{Cl}} = \frac{D_{K,\text{gel}}}{D_{Cl,\text{gel}}} = \frac{u_K}{u_{Cl}}. \quad (\text{B2})$$

Here D_K , D_{Cl} , and $D_{K,\text{gel}}$, $D_{Cl,\text{gel}}$ is the diffusion coefficient of the potassium and chloride ions in water and in the gel matrix, respectively. At 25 °C the ratio of the diffusion coefficients takes the value $r = 0.96$ [26]. Introducing this ratio r into formula (B1) and applying the condition of electroneutrality α can be expressed as

$$\alpha = \frac{(r+1)c_{K2} - a_F}{(r+1)c_{K1} - a_F}. \quad (\text{B3})$$

Inserting now the condition of Donnan equilibrium into the above equation gives α as a function of the fixed charge concentration a_F :

$$\alpha = \frac{\sqrt{1 + \left(\frac{2c_{02}}{a_F}\right)^2} + R}{\sqrt{1 + \left(\frac{2c_{01}}{a_F}\right)^2} + R}, \quad (\text{B4})$$

where

$$R = \frac{r-1}{r+1} = \frac{D_K - D_{Cl}}{D_K + D_{Cl}} = -0.02.$$

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