Hydrogels for Chemical Sensors

M. Guenther and G. Gerlach

Abstract A rapidly expanding field of on-line process monitoring and on-line control in biotechnology, food industry, pharmaceutical industry, process chemistry, environmental measuring technology, water treatment and sewage processing requires the development of new micro fabricated reliable chemical and biosensors that are specific for particular species and can attain the analytic information in a faster, simpler and cheaper manner. Using a functionalised hydrogel coating in sensors provides the possibility to detect, transmit and record the information regarding the concentration change or the presence of a specific analyte (a chemical or biological substance that needs to be measured) by producing a signal proportional to the concentration of the target analyte. In this chapter, we describe piezoresistive chemical microsensors for a comprehensive characterization of solutions, which could be embedded inside fluidic systems for real time monitoring of organic and inorganic contaminants.

Keywords Piezoresistive sensor • Biochemical sensor • Polyelectrolytic hydrogel • pH-sensitive • Temperature sensitive • Swelling behaviour

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Abbreviations

MBAAm	*N*,*N*′-methylene-bisacrylamide
DMAAm	Dimethylacrylamide
DMAEMA	*N*,*N*-dimethylaminoethyl methacrylate
DMIAAm	2- (dimethyl maleinimido)acrylamide
DMIMA	2-(dimethyl maleinimido)ethyl methacrylate
EDTA	Ethylene diamine tetra-acetic acid
NIPAAm	*N*-Isopropylacrylamide
NMRP	Nitroxide mediated radical polymerization
PAAc	Poly(acrylic acid)
PBS	Phosphate buffer saline
PECVD	Plasma enhanced chemical vapour deposition
PVA	Poly (vinyl alcohol)
P2VP	Poly (2-vinylpyridine)
P4VP	Poly (4-vinylpyridine)

Symbols

B	Viscosity coefficient in Jones-Dole expression
c_g	Concentration of ionizable groups on the polymer backbone
c_{gi}	Concentration of ionized groups on the polymer backbone
c_α	Additive concentration in the gel
c_α^0	Additive concentration in the surrounding solution
D_α	Effective diffusion coefficient of the additive
d	Thickness of the swollen gel layer
d_d	Thickness of the dry gel layer
F	Faraday constant

f	function
I	Ionic strength
k	Equilibrium constant of the reaction: $k=k_f/k_b$
k_b	Backward reaction rate constant
k_f	Forward reaction rate constant
M_n	Molecular weight
p	Pressure
pK_a	Acid exponent
R	Universal gas constant
r	Resistance
S	Sensitivity
T	Absolute temperature
T_{cr}	Volume phase transition temperature (critical temperature)
t	Time
U_{out}	Output voltage
V	Volume of the hydrogel
$V_{M,\alpha}$	Molar volume of the additive
v	Initial slope of the swelling curve
w	Deflection
x	Coordinate
z_i	Valence of i-th ionic species
Δ	Difference
ε	Strain
ε_0	Permittivity of vacuum
ε_1	Relative dielectric constant of the solvent
η	Viscosity
μ_i	Chemical potential of component i
ν_c	Cross-linking degree
π	Osmotic pressure
Ψ	Electrical potential
σ	Stress
τ	Time constant

Indices

a	Acid
b	Backward
c	Cross-linking
cr	Critical
d	Dry
eq	Equilibrium
f	Forward
g	Gel
α	Additive, species

1 Hydrogel-Based Piezoresistive Chemical Sensors

"Stimuli-responsive" or "smart" gels have attracted particular attention in the novel and most intensively developing field of polymers with sensor-actuator functions. The sensitivity of hydrogels to a large number of physical factors like temperature (Kuckling et al. 2003a; Richter et al. 2004a), electrical voltage (Richter et al. 2003; Wallmersperger 2003, Wallmersperger et al. 2004), pH (Kuckling et al. 2003a; Wohlrab and Kuckling 2001; Oktar et al. 2005), concentration of organic compounds in water (Arndt et al. 2000; Saito et al. 1993; Kumar et al. 2006; Orakdogen and Okay 2006), and salt concentration (Saito et al. 1993; Panayiotou and Freitag 2005; Liu et al. 2003; Cong et al. 2002) make them promising materials for a broad range of applications as microsensors (Liu et al. 2003; Cong et al. 2002; Richter et al. 2004b; Bashir et al. 2002; Lei et al. 2006; Herber et al. 2004; Gerlach et al. 2004; Gerlach et al. 2005; Guenther et al. 2005, 2006, 2007a, 2007b, 2007c, 2008) and microactuators (Kuckling et al. 2003a; Richter et al. 2004a; Richter et al. 2003; Arndt et al. 2000) in MEMS devices.

Stimuli-responsive hydrogels are capable of reversibly converting chemical energy into mechanical energy. That makes them very useful as sensitive material for chemical and biosensors. The following principles for the detection of environmental parameters are used in sensors based on the swelling behavior of hydrogels:

- Changes of the holographic diffraction wavelength in optical Bragg-grating sensors (Liu et al. 2003; Cong et al. 2002)
- Shifts of the resonance frequency of a quartz crystal microbalance in microgravimetric sensors (Richter et al. 2004b)
- Bending of micromechanical bilayer cantilevers (Bashir et al. 2002)
- Deflection of a membrane, or bending plate[1] in capacitor/inductor micromachined resonator (Lei et al. 2006) and in piezoresistive pressure sensors (Herber et al. 2004; Gerlach et al. 2004; Gerlach et al. 2005; Guenther et al. 2005, 2006, 2007a, 2007b, 2007c, 2008)

In the following, we describe a chemical sensor combining a smart hydrogel and a micro fabricated pressure sensor chip for continuously monitoring the analyte-dependent swelling of a hydrogel in aqueous solutions.

1.1 Operational Principle

Figure 1 illustrates the operational principle of hydrogel-based sensors. Pressure sensor chips with a flexible thin silicon bending plate and with an integrated piezoresistive Wheatstone bridge inside this plate have been employed as

[1] Bending plates are characterized by bending deformations, whereas in membranes tensile stress dominates instead of bending stresses. Nevertheless, bending plates are often called membranes.

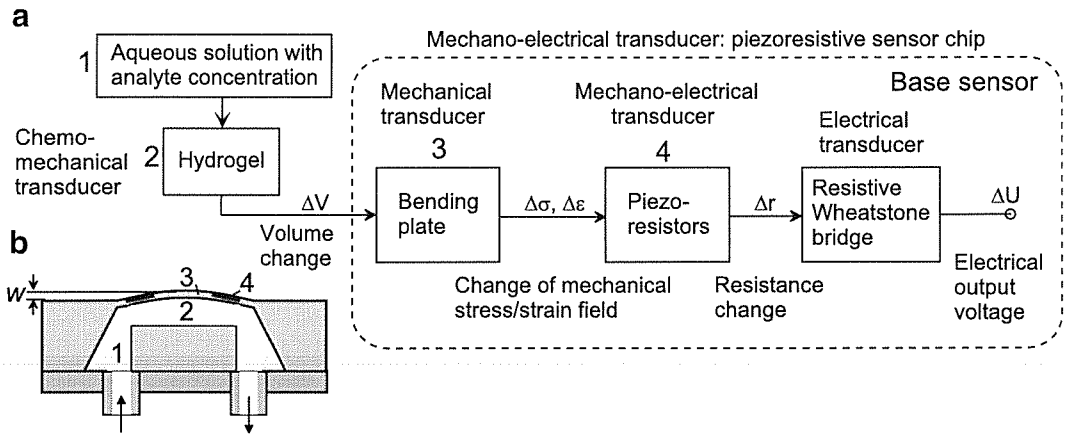


Fig. 1 Operational principle (a) and cross-section (b) of hydrogel-based chemical sensor: 1 measuring solution; 2 hydrogel; 3 Si bending plate; 4 piezoresistors

mechano-electrical transducer for the transformation of the plate deflection w into an appropriate electrical output signal U_{out}.

The aqueous solution to be measured is pumped through the inlet channels into the chip cavity and induces swelling or shrinking processes of the hydrogel inside the chip cavity. These processes were monitored by corresponding changes in the piezoresistance of an integrated Wheatstone bridge inside a rectangular silicon plate. The plate deflection causes a stress state change inside the plate and therefore a resistivity change of the resistors affecting proportionally the output voltage U_{out} of the sensor (German Patents DE 101 29 985C2, DE 101 29 986C2, DE 101 29 987C2, June 12 2001). An increase of U_{out} corresponds to the hydrogel swelling whereas a reduction of the electric output voltage corresponds to the shrinkage of the gel.

1.2 Sensor Design

For the design of the chemical sensor, commercially available pressure sensor chips (AktivSensor GmbH, Stahnsdorf, Germany) were used. The hydrogel itself was brought into a cavity at the backside of the silicon chip and was closed with a cover. This cavity on the backside of the chip was wet etched with a silicon nitride mask as etch resist. Therefore, only the backside of the chip came in contact with the measuring species, whereas the front side carrying the electronic components was strictly protected from it. Since the sensor chips show excellent stable properties, the long-term stability of the sensor is solely determined by the stability of the hydrogel characteristics.

The sensor chip was bonded to a socket with inlet and outlet flow channels. The aqueous solution to be measured was pumped through the inlet tubes into the silicon chip cavity coated with a 220 nm thick PECVD silicon nitride film to provide chemical protection. In the present work, three sensor designs have been used:

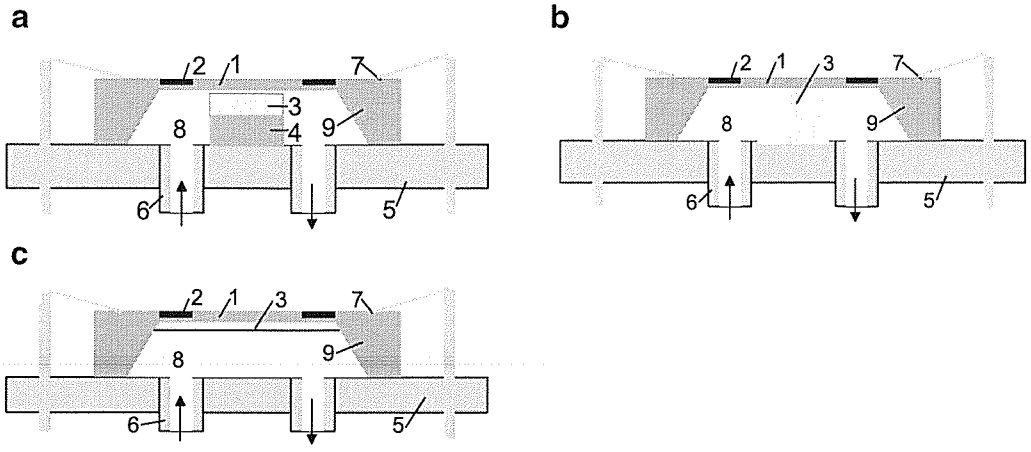


Fig. 2 Design variants of hydrogel-based sensors: 1 bending plate; 2 mechano-electrical transducer (piezoresistive bridge); 3 swellable hydrogel; 4 Si substrate (5 mm x 5 mm x 0.3 mm); 5 socket ; 6 tube ; 7 interconnect; 8 solution; 9 Si chip (5 mm x 5 mm x 0.4 mm). Reprinted from (Gerlach et al. 2004; Gerlach et al. 2005; Guenther et al. 2005, 2006, 2007b) with kind permission from Elsevier, Wiley-VCH and SPIE

- In order to obtain a sufficient measuring signal, a 50...100 μm thick hydrogel layer is located on a silicon platform to achieve a small enough gap between dry (absolutely unswollen) hydrogel and the silicon bending plate (Fig. 2a). The hydrogel layer was spin-coated on the Si wafer, which was covered with a 550 nm thick silicon oxide layer and with a 17 nm thick adhesion promoter layer, dried and then cross-linked.
- A 250 μm thick cross-linked and dried hydrogel foil was cut into pieces of 1 mm x 1 mm. A piece of foil was glued to a socket inside the chip cavity (Fig. 2b).
- In order to improve the sensor response time, a thin hydrogel layer was directly deposited onto the backside of the bending plate covered with a 220 nm thick PECVD silicon nitride film and with a 17 nm thick adhesion promoter layer (Fig. 2c). The final thickness of the dried and then cross-linked hydrogel layer was 4...50 μm.

1.3 Sensor Calibration

The calibration curves $w=f(p)$, $w=f(U_{\text{out}})$, and $p=f(U_{\text{out}})$ of the sensor have been obtained by using the controller of the pressure p to deflect a 20 μm thick silicon plate (Fig. 3). The silicon plate deflection w has been measured by means of a two-beam laser interferometer (Guenther et al. 2007a, 2008). The regression equations w (μm) vs. U_{out} (mV) and p (kPa) vs. U_{out} (mV) were obtained by fitting with the experimental curves as

$$w = 3.4 + 0.1U_{out} + 7.7 \times 10^{-4}U_{out}^2, \tag{1}$$

$$p = -0.8 + 4.14\exp(U_{out}/52.7). \tag{2}$$

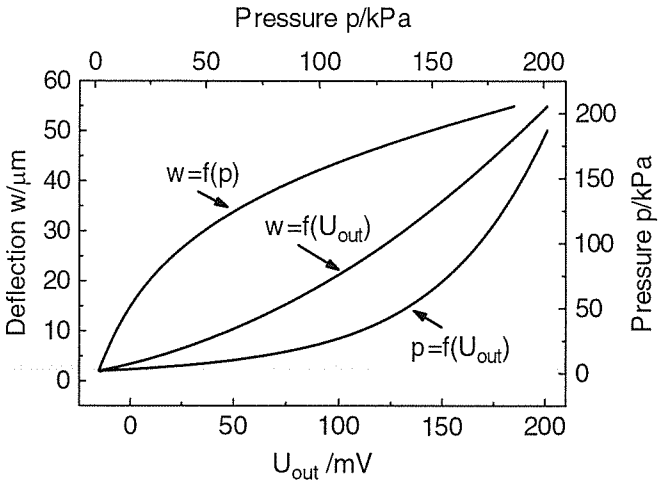


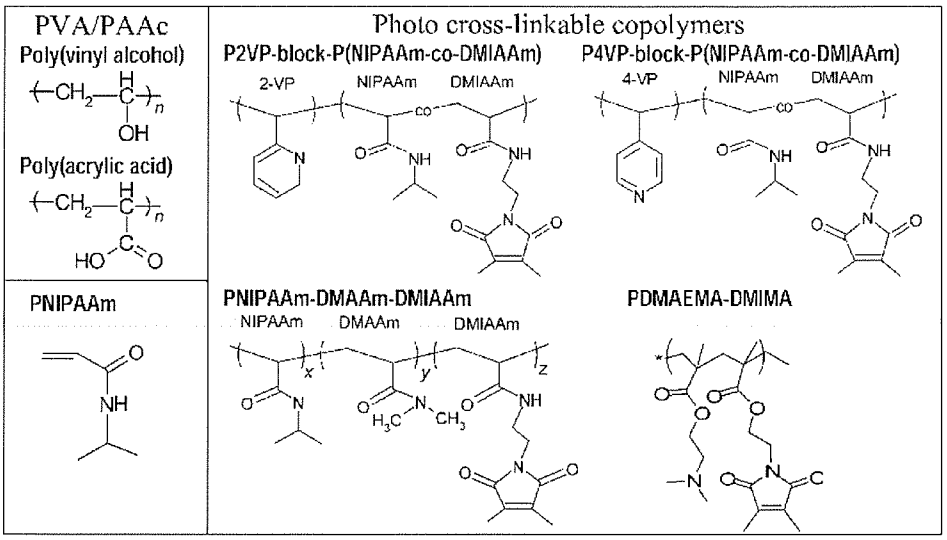
Fig. 3 The calibration curves $w=f(p)$, $w=f(U_{out})$, and $p=f(U_{out})$ of the chemical sensor. Reprinted from (Guenther et al. 2008) with kind permission from Elsevier

2 Hydrogel Material Preparation and Characterization

The following cross-linked hydrogel systems were used in the present work (Table 1):

- *Poly(vinyl alcohol)/poly(acrylic acid) (PVA/PAAc) blends*: The swelling degree of these polyanionic hydrogels changes steeply with the change of the pH value of the measuring species: it is at minimum in acids and takes its maximum in bases (Arndt et al. 1999).
- *N-Isopropylacrylamides (NIPAAm)*: PolyNIPAAm (PNIPAAm) is one of the best-studied thermo-responsive materials. PNIPAAm gel contains hydrophilic amino and carbonyl groups as well as hydrophobic isopropyl groups and exhibits large and sharp changes in its swellability in water upon raising the temperature above its volume phase transition temperature T_{cr}=33 °C. The thermally induced reversible collapse of PNIPAAm can be controlled by the use of mixed solvents (Arndt et al. 2000; Saito et al. 1993; Kumar et al. 2006; Orakdogen and Okay 2006; Guenther et al. 2006, 2008), addition of salts (Saito et al.7 1993; Panayiotou and Freitag 2005; Guenther et al. 2006, 2007b, 2008), addition of metal ions (Oktar et al. 2005; Guenther et al. 2007b, 2007c, 2008; Kuckling and Pareek 2003), or addition of surfactants (Caykara et al. 2006) that results in a T_{cr}–shift. Practical applications of PNIPAAm usually involve its chemical modification which has been achieved by its co-polymerization with anionic (Oktar et al. 2005; Harmon et al. 2003), neutral (Harmon et al. 2003; Kuckling et al. 2002), and cationic (Wohlrab and Kuckling 2001; Harmon et al. 2003) monomers. Changes in the polymer composition have allowed to vary the gel volume phase transition temperature (T_{cr}) from 25° to 58°C (Wohlrab and Kuckling 2001; Kuckling et al. 2002; Kuckling et al. 2000). The micro-fabricated thermo-responsive hydrogels have been prepared using a photolithographic patterning of photo cross-linkable PNIPAAm polymers (Kuckling et al. 2003b; Hoffmann et al. 1999). Scaling to microdimensions is very effective

Table 1 Chemical structure of the used hydrogels



in decreasing the response time. The possibility for an enhancement of the gel's time response is particularly relevant for applications of smart hydrogels in microsystems.

- *Copolymer of N,N-dimethylaminoethyl methacrylate (DMAEMA)*: This polycationic pH- and temperature-sensitive gel possesses specific coordination binding sites for transition-metal ions.

2.1 *Thermally Cross-Linked Poly(vinyl Alcohol)/ Poly(Acrylic Acid) Blend*

PVA and PAAc polymers obtained from Aldrich Chemical Co. were dissolved separately in distilled water under stirring at 80°C (PVA 15 wt% and PAAc 7.5 wt%). For hydrogel formation, the solutions are then mixed in such a manner that 80 wt% were PVA and 20 wt% PAAc. This mixture is stirred for 1 h at 60°C to manufacture a homogeneous solution (Arndt et al. 1999). The films of PVA/PAAc blends were deposited onto the Si wafer (Fig. 2a) or onto the backside of the silicon bending plate (Fig. 2c). A solution of α-amino propyltriethoxysilane was used as adhesion promoter. Finally, the dried hydrogel films were isothermally annealed in an oven at 130°C for 20 min.

2.2 *Chemically Cross-Linked* N*-Isopropylacrylamide*

The cross-linked PNIPAAm hydrogels were prepared according to (Arndt et al. 2000) by free radical polymerization of NIPAAm in water with *N,N′*-methylene-bisacrylamide (MBAAm; MBAAm content: 4 mol%) as the cross-linking agent. A solution of

NIPAAm, MBAAm (overall monomer concentration 0.53 mol/l) and potassium peroxodisulfate as initiator (3×10^{-3} mol/mol monomer) were cooled to 0 °C and purged with nitrogen for 15 min. *N*,*N*,*N*',*N*'-tetramethylethylenediamine as accelerator (3×10^{-3} mol/mol monomer) was added and the solution was immediately transferred into a Petri dish to get hydrogel foils. After 17 h reaction time at 20°C, the gels were separated and washed with water for 1 week. For PNIPAAm chemical sensors, 250 µm thick hydrogel foil pieces were used (Fig. 2b). The dried PNIPAAm foils were prepared by evaporation of water at room temperature and then cut into pieces of 1 mm × 1 mm. The hydrogel was glued to a socket as a piece of foil.

2.3 Photo Cross-Linkable Copolymers

In order to prepare thin hydrogel layers, photo cross-linkable copolymers were used.

2.3.1 Materials

N-isopropylacrylamide (NIPAAm, ACROS) was purified by recrystallisation from hexane and afterwards dried in vacuum. 2-vinylpyridine 98 % (2VP, Merck) was stirred over calcium hydride for 24 h and distilled over calcium hydride. Diethyl ether, ethyl acetate, dioxane, and tetrahydrofuran (THF) were distilled over potassium hydroxide. Dimethylformamide (DMF), cyclohexanone were purified by distillation over calcium hydride. 2,2´-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. All other reagents were of analytical grade. The 2-(dimethylmaleinimido)acrylamide (DMIAAm) monomer was synthesized according to (Vo et al. 2002). 1-[3-(chloro-dimethyl-silanyl)-propyl]-3,4-dimethylmaleimide was prepared according to (Kuckling et al. 2003b). The synthesis of *N*-tert-butyl-*N*-(2-methyl-1-phenyl-propyl)-*O*-(1-phenyl-ethyl)-hydroxylamine and the corresponding nitroxide 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxyl (TIPNO) is described in (Krause et al. 2004; Benoit et al. 1999).

2.3.2 P2VP-block-P(NIPAAm-co-DMIAAm) block copolymer

This polymer was synthesized via NMRP (Nitroxide Mediated Radical Polymerization) (Benoit et al. 1999) by sequential polymerization of 2VP and a mixture of NIPAAm and DMIAAm. Using the macroinitiator method, the preparation of well-defined linear block copolymers consisting of a homo polymer block P2VP (pH-sensitive) and a random copolymer block of PNIPAAm (temperature sensitive) with DMIAAm (photo crosslinker) was possible.

A mixture of 3.5 ml (0.032 mol) 2VP, 100 µl acetic anhydride, and 0.125 g (0.38 mmol) of the alkoxyamine was degassed by three freeze/thaw cycles, sealed under

argon, and heated at 110 °C for 6 h. After that the polymerization was stopped by freezing with liquid nitrogen. The reaction mixture was then diluted with THF and precipitated in n-pentane. The powder was dried in vacuum to give the desired alkoxyamine-terminated P2VP.

A mixture of 0.25 g (1.1 mmol) alkoxyamine-terminated P2VP macroinitiator, 3.5g (0.33 mol) NIPAAm, DMIAAm (5 mol%/mol monomer), TIPNO (0.5 mol%/mol macroinitiator) dissolved in 3.5 ml DMF was degassed by three freeze/thaw cycles, sealed under argon and heated at 135°C for 48 h. The reaction was stopped by liquid nitrogen. The solvent was evaporated under reduced pressure. The concentrated mixture was redissolved in chloroform and precipitated in cold diethylether. The resulting brownish powder was dried in vacuum. To remove the unreacted P2VP, the polymer was purified by dialysis in THF using a Spectra/Por membrane.

2.3.3 PNIPAAm-DMAAm-DMIAAm terpolymer

This PNIPAAm copolymer was obtained by free radical polymerization of NIPAAm, dimethylacrylamide (DMAAm) and DMIAAm initiated with AIBN at 70 °C in dioxane with a total monomer concentration of 0.55 mol/l under nitrogen for 7 h. The polymer was precipitated in diethylether and purified by reprecipitation from THF into diethylether (1:3).

2.3.4 PDMAEMA-DMIMA copolymer

This copolymer was obtained by free radical polymerization of *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA) and 2-(dimethyl maleinimido)ethyl methacrylate (DMIMA) as the chromophore initiated with AIBN at 70 °C in ethylmethylketone for 7 h. The polymer was precipitated in *n*-pentane and purified by reprecipitation from ethylmethylketone into *n*-pentane (1:8).

2.3.5 Polymer characterization

The molecular weight (M_n) of the copolymers was determined by gel permeation chromatography (GPC) with a PL120 instrument equipped with RI detector using PSS "GRAM" columns. The samples were measured at 50 °C in dimethylacetamide (DMAc) containing 0.42 g/l lithium bromide as mobile phase with a flow rate of 1 ml/min. The molecular weight of the copolymers was about 44.6 kg/mol for P2VP-block-P(NIPAAm-co-DMIAAm) and 29.0 kg/mol for PNIPAAm-DMAAm-DMIAAm (Table 2). The molecular weight M_n=26 kg/mol of the PDMAEMA-DMIMA copolymer was determined by GPC with a JASCO instrument equipped with UV and RI detector using Waters "Ultrastyragel" columns. The samples were measured against 3,5-di-*tert*-4butylhydroxytoluene (BHT) standard at 30 °C in chloroform containing 0.1 vol% triethylamine as the mobile phase with a flow rate of 1 ml/min.

Table 2 Chemical composition, molecular weight M_n, and phase transition temperature T_{cr} of the used photo cross-linkable hydrogels. Reprinted from (Guenther et al. 2007b, 2007c, 2008) with kind permission from Elsevier, Wiley-VCH and SPIE

Gel	Chemical composition, mol%							M_n,	T_{cr}, °C
	P2VP	NIPAAm	DMIAAm	P4VP	DMAAm	DMAEMA	DMIMA	kg/mol	
1a	18.9	73.1	8.0					44.6	25
1b	21.9	72.9	5.2					41.5	
2a		79.9	5.6	14.5				45.0	22
2b		62.6	8.6	21.0				28.8	
3		66.3	3.0		30.7			29.0	43
4						90.2	9.8	25.6	33.5

The chemical composition of the copolymers was determined by ^{1}H NMR (Table 2). The ^{1}H NMR spectra were recorded on a BRUKER DRX 500 spectrometer (500 MHz). The solvent was used as an internal reference.

The phase transition temperature of the 5 wt% aqueous polymer solution was determined by DSC with a TA Instruments DSC 2920. The P2VP-block-P (NIPAAm-co-DMIAAm) block copolymer has a lower value of T_{cr} (T_{cr}=25 °C) than PNIPAAm (T_{cr}=33 °C) due to the additional hydrophobic P2VP and DMIAAm components whereas the PNIPAAm-DMAAm-DMIAAm terpolymer has a higher value of T_{cr} (T_{cr}=43 °C) than PNIPAAm due to the additional hydrophilic DMAAm component (Table 2).

2.3.6 UV Cross-Linking

The DMI-chromophore was selected for cross-linking because it is known to form stable dimers. The DMI-chromophore reacts via a [2+2]-cycloaddition under irradiation. By using thioxanthone as photo sensitizer, a complete conversion of the chromophores could be achieved within a few minutes (Kuckling et al. 2003b).

The adhesion promoter layer was prepared by absorbing 1-[3-(chloro-dimethyl-silanyl)-propyl]-3,4-dimethylmaleimide from 0.3 vol% solution in dicyclohexyl on Si/Si_3N_4 surface of the chip bending plate for 24 h. The substrates were rinsed with chloroform. Photo cross-linkable polymer films were deposited by pipetting of 3 µl cyclohexanone solution containing 10 wt% polymer and 2 wt% (with respect to the polymer) thioxanthone sensitizer (Guenther et al. 2007b). The PDMAEMA-DMIMA copolymer was dissolved in ethylmethylketone. The films were dried at 60 °C for 15 min and then under vacuum at 20 °C for 5 min. The dry films were cross-linked by UV irradiation, using a mercury lamp producing an irradiance at the substrate plane of 1.7 mW/cm^2. The resulting dry film thicknesses ranged from 4 to 6 µm.

2.4 Hydrogel Conditioning

After the sensor preparation, an initial gel conditioning procedure was performed. A corresponding initial gel swelling in de-ionized water at low temperature ($T<T_{cr}$)

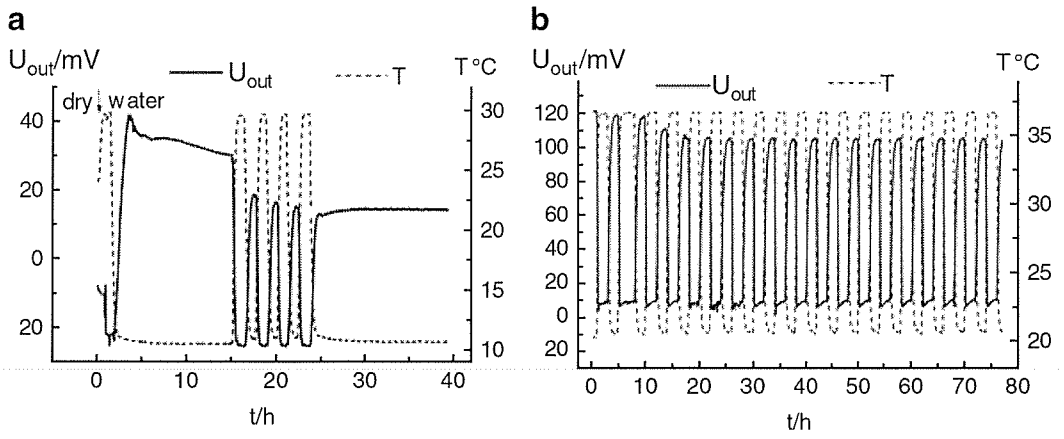


Fig. 4 Initial gel conditioning procedure in de-ionized water for (a) P2VP-block-P(NIPAAm-co-DMIAAm) (Gel 1a in Table 2) (Guenther et al. 2007c) and (b) PNIPAAm (MBAAm 4 mol%) (Guenther et al. 2006). Reprinted with kind permission from Wiley-VCH and SPIE

for 24 h preceded the deswelling/swelling cycling at increasing/decreasing temperature. During the first operation the hydrogel sensor often shows a poor repeatability and a drift of the sensor parameters. This phenomenon is caused by changes in the microscopic structure of the polymer network. It was found that the stability of the sensitivity (Fig. 4a) and the repeatability (Fig. 4b) can be significantly increased by performing a number of conditioning cycles. The conditioning process was accomplished after 5...7 swelling cycles. The sensor's output voltage was measured during the swelling/deswelling of the hydrogel layer under variable, tightly controlled ambient conditions. The temperature was controlled with a Vaisala HMP 230 humidity and temperature sensor with an uncertainty $\Delta T = \pm 0.1\ K$. An uncertainty of the temperature setting was $\Delta T = \pm 0.5\ K$. The solution was pumped with a flow rate of 0.8 ml/min.

2.5 *Temperature Sensitivity of PNIPAAm Gels*

The thermo-shrinking cross-linked copolymers of PNIPAAm were investigated as a functionalised polymer coating in chemical sensors using an appropriate measuring setup. The gel, initially swollen in water at room temperature, shrinks with increasing temperature. The volume phase transition of PNIPAAm occurs at 33 °C (Fig. 5a, 1). Changes in the polymer composition have allowed to vary the gel volume phase transition temperature (T_{cr}) from 22 °C to 25 °C for P4VP-block-P(NIPAAm-co-DMIAAm) and P2VP-block-P(NIPAAm-co-DMIAAm), respectively to 43 °C for PNIPAAm-DMIAAm-DMAAm terpolymer (Fig. 5a and Table 2). Fig. 5b demonstrates that a sufficiently high long-term stable sensitivity of the PNIPAAm gel in chemical sensors is maintained during the several years under the specific measurement and storage conditions (see Sect. 3.3).

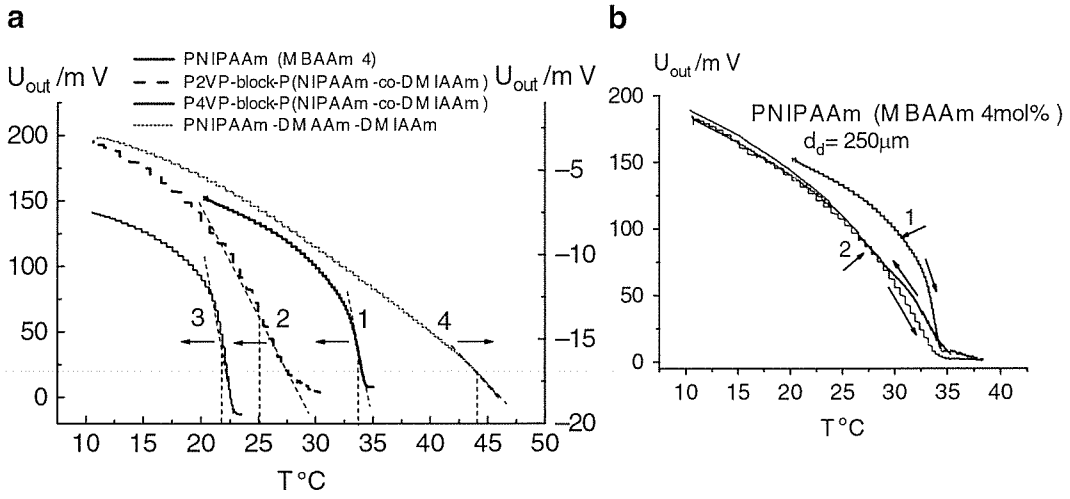


Fig. 5 Sensor output voltage in dependence on temperature: (a) for PNIPAAm (MBAAm 4) (1), P2VP-block-P(NIPAAm-co-DMIAAm) (2), P4VP-block-P(NIPAAm-co-DMIAAm) (3), and PNIPAAm-DMAAm-DMIAAm (4) in water; (b) for PNIPAAm (MBAAm 4) after sensor preparation (1) and after 2.8 working years of the sensor (2)

3 pH Sensors

The swelling ability of pH-sensitive polyelectrolyte hydrogels depends on the functional acidic or basic groups at the polymer backbone. Due to the dissociation of these groups and the influx of counterions, the concentration of ions in the hydrogel is higher than in the surrounding solution. This causes a difference in osmotic pressure and results in a solution flux into the hydrogel and, consequently, a swelling. The interaction and repulsion of charges along the polymer chain also lead to an increased swelling. Quasi-equilibrium of ionic gels occurs when the elastic restoring force of the polymer network balances the osmotic forces. During the swelling process of PVA/PAAc at pH values near and above the acid exponent of acrylic acid ($pK_a = 4.7$), hydroxide ions are transported into the neutral gel, while during the shrinkage protons diffuse into the gel and neutralize the negatively charged acidic carboxylate groups. This ion diffusional flux induces an electrical potential difference that drives the electromigration of the ions in the direction opposite to that of the diffusion. After the time t_{eq}, the quasi-equilibrium between the gel and the solution is reached. In the so called Donnan quasi-equilibrium state, the diffusional flux of the ions in one direction is equal to the electromigrational flux in the opposite direction, resulting in a net nearly zero mass transport and a net nearly zero charge transport.

The concentration $c_{\alpha,eq}$ of the ionic additive in the gel after the time t_{eq} differs from that one in the surrounding solution c_α^0 and is determined by a Donnan quasi-equilibrium condition as

$$c_{\alpha,eq} = c_\alpha^o \exp\left[-(z_\alpha F\Delta\Psi + \pi V_{M,\alpha} + \Delta\mu_\alpha^0)/RT\right]. \quad (3)$$

Here, $\Delta\Psi$ is the electrical Donnan potential at the gel-solution interface, π the osmotic pressure, $V_{M,\alpha}$ and $\Delta\mu_\alpha{}^0$ denote the additive molar volume and the difference between the additive standard chemical potentials in the gel and in the solution, respectively, and z_α the charge on the additive ion. The other notations are: R the universal gas constant, T the absolute temperature, and F the Faraday constant.

The electrical potential Ψ is described by the Poisson-Boltzmann equation

$$\Psi_{,xx} = -\frac{\mathrm{F}}{\varepsilon_1 \varepsilon_0}\left[z_g c_{gi} + \sum_i z_{\alpha_i} c^0_{\alpha_i} \exp\left(-\frac{z_{\alpha_i} e\Psi}{kT}\right)\right] \tag{4}$$

and by the charge neutrality condition inside the gel

$$z_g c_{gi} + \sum_i z_{\alpha_i} c_{\alpha_i} = 0. \tag{5}$$

Here, z_g is the charge on the ionized groups with the concentration c_{gi}, ε_0 the permittivity of vacuum, and ε_1 the relative dielectric constant of the solvent.

In order to realize pH sensors, the weak polyelectrolyte anionic PVA/PAAc as well as cationic P2VP-block-P(NIPAAm-co-DMIAAm) and P4VP-block-P (NIPAAm-co-DMIAAm) gels with a pH-value dependent swelling behaviour were used as chemo-mechanical transducers. Since P2VP and P4VP are weak polycations, their backbone charge increases as the solution pH is lowered. At pH < 6.7, P2VP is protonated (Houbenov et al. 2003) and a further decreasing of pH results in an increasing density of positive charges on the P2VP chains. For the sensor signal calibration, buffered solutions of 0.2 M ionic strength were used which varied between pH values of 1 and 11.

3.1 Sensitivity

Beside response time, stability and selectivity, the sensitivity is one of the most crucial parameters for a successful sensor implementation. The sensitivity $S = \Delta U_{out}/\Delta pH$ of a pH sensor is determined by the polymer composition (the concentration c_g of the ionizable groups in the gel) as well as by its cross-linking degree ν_c. The latter depends on the content of the cross-linking agent in the polymer as well as on the UV irradiation conditions for the photo cross-linkable hydrogel. Fig. 6 (curves 1 and 2) shows the output characteristics obtained for sensors with P2VP-block-P(NIPAAm-co-DMIAAm) hydrogel layers of the same polymer composition, but with different cross-linking degrees ν_{c1} and ν_{c2} ($\nu_{c1} < \nu_{c2}$) due to different irradiation conditions (different irradiation times t_1 and t_2, $t_1 < t_2$). As consequence, $S_1 = 12.5$ mV/pH is higher than $S_2 = 8$ mV/pH. All measurements were performed with a signal resolution of 0.08 mV. For 4 μm thick photo-cross-linked hydrogel layers as well as for thermally cross-linked PVA/PAAc layers with a thickness of

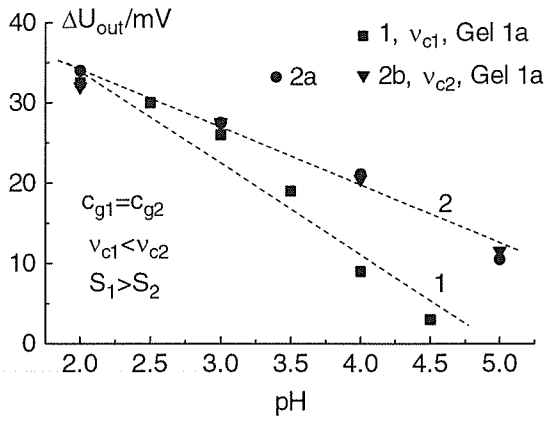


Fig. 6 Output characteristics of the pH-sensors with P2VP-block-P(NIPAAm-co-DMIAAm) gel

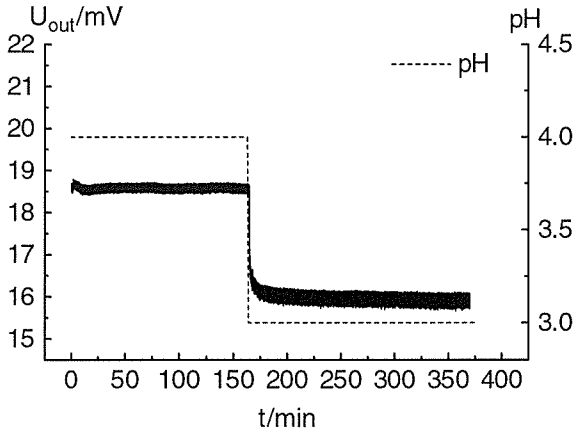


Fig. 7 Sensor output voltage during the deswelling process of PVA/PAAc from pH4 to pH3. Reprinted from (Guenther et al. 2005) with kind permission from SPIE

Table 3 Parameters of pH sensors with voltage, frequency, pressure or deflection output, respectively. Reprinted from (Guenther et al. 2007b) with kind permission from Elsevier

Hydrogel	Sensitivity, per pH unit	Signal resolution	Response time, s	Thickness of gel layer, μm	pH range	References
P2VP-block-P (NIPAAm-co-DMIAAm)	12.5 mV	0.08 mV	70	4	2–5	(Guenther et al. 2007b)
PVA/PAAc	2.5 mV	0.16 mV	90	6	3–4	(Guenther et al. 2005)
PVA/PAAc	13.2 kHz	0.62 kHz	0.5	0.39	2.55–3.45	(Richter et al. 2004b)
DMAEMA-co-HEMA	60 kPa	2 kPa	600	10	6–7.5	(Herber et al. 2004)
PMAA-PEGDMA-DMPA	18.3 μm	0.01 μm	70	2.5	5.9–6.7	(Bashir et al. 2002)

6 μm (Fig. 7) (which were directly deposited on the backside of the bending plate), a sufficient sensitivity has been obtained. For a comparison, the parameters achieved for hydrogel-based pH sensors are listed in Table 3.

3.2 Response Time

Because the gel response is typically diffusion-driven, the time response of the volume change approximately follows the square of the sample dimension. Scaling to micro-dimensions enhances the time response. Consequently, a reduction of the sample size improves the sensor performance. Time constants down to a few ten seconds have been found for thin hydrogel layers deposited directly on the backside of the bending plate (Table 3 and Fig. 8). However, a reduction of the gel thickness is limited by the necessity to obtain a sufficiently high sensor signal and consequently, a sufficient sensitivity. In order to achieve an optimum between the sensor signal amplitude and the sensor response time, the swelling/deswelling kinetics of the polyelectrolyte hydrogel was investigated (Gerlach et al. 2005; Guenther et al. 2005, 2007a, 2007b).

The several processes occur simultaneously during the hydrogel swelling in the solution with the additive concentration $c_\alpha{}^0$:

- Diffusion of the additive into the gel. The concentration c_α of the additive in the gel depends on the distance x from the gel surface and increases with the time as (Crank 1970)

$$c_\alpha = c_{\alpha 0} + (c_\alpha^0 - c_{\alpha 0})\left[1 - \mathrm{erf}(x/2\sqrt{D_\alpha t})\right], \tag{6}$$

where $c_{\alpha 0}$ is the initial additive concentration in the gel, D_α the effective diffusion coefficient of the additive, and $\mathrm{erf}(\delta)$ the error or probability function, given by

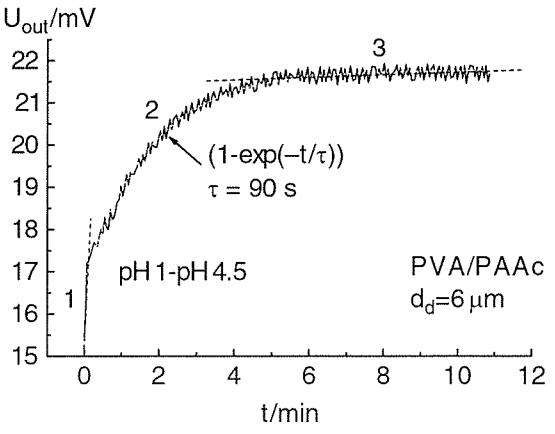


Fig. 8 Sensor output voltage during the swelling process of PVA/PAAc from pH1 to pH4.5. Reprinted from (Gerlach et al. 2005; Guenther et al. 2005) with kind permission from Elsevier and SPIE

$$\mathrm{erf}(\delta) = \frac{2}{\sqrt{\pi}} \int_0^{\delta} e^{-\varsigma^2} d\varsigma. \tag{7}$$

- This additive concentration sparks off the ionization process in the gel with a rate

$$\dot{c}_{gi} = k_f c_\alpha (c_g - c_{gi}) - k_b c_{gi}, \tag{8}$$

where c_{gi} and c_g are the concentrations of the ionized and ionizable groups on the polymer backbone, respectively, k_f and k_b the forward and backward reaction rate constants, respectively. The backbone charge increases because of the ionization and leads to an increase of the gel hydrophilicity and consequently to additional water uptake.

- Additional water uptake. The amount of the absorbed water steadily increases due to the steadily increasing amount of ionized polymer groups induced by the additive (Gerlach et al. 2005; Guenther et al. 2007a).

The polymer chain relaxation rate is much slower than the diffusion rates of the additive and water. This leads to the retarded gel swelling which is limited by a relaxation process with the time constant τ (Fig. 8). It was found that the total amount of the additionally absorbed water as well as the rate of the initial rapid swelling (Fig. 8,1) and the rate of the slow long-time drift (Fig. 8,3) depends on the initial concentration gradient ($c_\alpha{}^0$- $c_{\alpha 0}$) of the additive between the solution and the gel (Gerlach et al. 2005; Guenther et al. 2007a). In order to shorten the sensor response time, the dependence of the rate v of the initial solution sorption on the initial concentration gradient can be used (Guenther et al. 2008). With the help of the values v_1 and v_2 for two solutions with a known concentration $c_{\alpha,1}{}^0$ and with an unknown one $c_{\alpha,2}{}^0$, the value of $c_{\alpha,2}{}^0$ can be estimated as

$$\lg(c^0_{\alpha,2} - c_{\alpha 0,2}) = \lg(c^0_{\alpha,1} - c_{\alpha 0,1}) + \lg(v_2/v_1). \tag{9}$$

Fig. 9a demonstrates the swelling curves for a thick PVA/PAAc layer (d_d=50 μm) in buffer solutions with different pH values. The values of U_{out} were recalculated in terms of the change Δd of the gel layer thickness using Eq. (1) and taking into account that $\Delta d \approx w$ (Fig. 9b). The values of the initial slope obtained from Fig. 9b and the values of the hydroxide ions concentration estimated using Eq. (9) are listed in Table 4. One sees that the estimated values of $c_{OH^-}{}^0$ are in good agreement with the concentration values used in the experiment. By applying this method, the measuring time which is necessary to determine the additive concentration in a solution is essentially shortened from the time t_{eq} (to reach a full saturation of the solution uptake) to the time t_m which is necessary for the initial slope determination (Table 5).

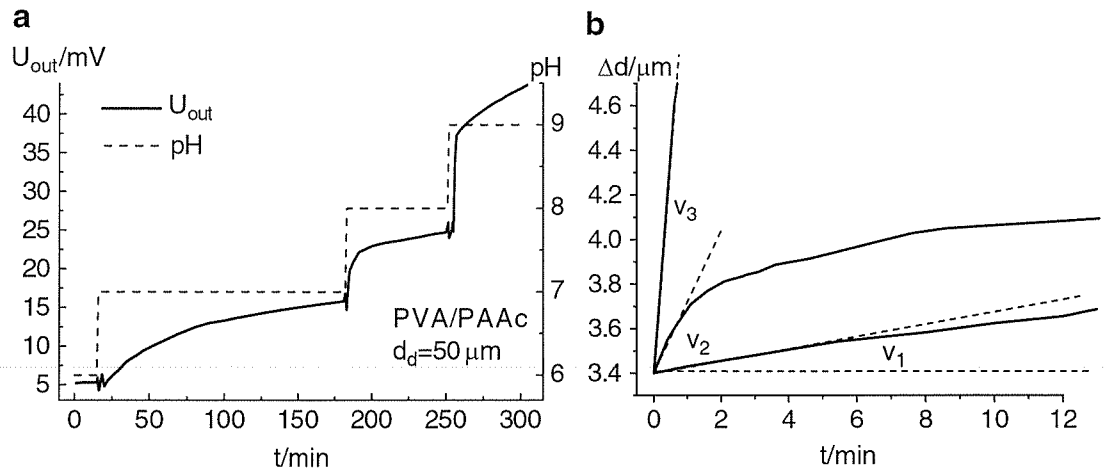


Fig. 9 Output voltage U_{out} of a pH sensor (a) and corresponding change Δd of the PVA/PAAc layer thickness (b) during the gel swelling in solutions with different pH values.

Table 4 Values of the initial slope v of the hydrogel swelling curves and corresponding calculated values of the OH^- concentration

pH	v, µm/min	lg $c_{OH^-}{}^0$
6		-8
7	0.02	-7
8	0.32	-6
9	1.75	-5

Table 5 Values of the equilibrium and measuring times t_{eq} and t_m for the kinetics curves of the 50 µm thick PVA/PAAc layer in the investigated solutions

pH	t_{eq}, min	t_m, min
7...11	>180	6
6...7	>150	6
7...8	>70	1
8...9	>50	0.5

3.3 Signal Reproducibility

Of particular interest is the reproducibility of repeated pH measurements under a specific set of conditions. It was found that a hysteresis in the output characteristic of a pH sensor is observed complicating the calibration procedure and affecting the signal reproducibility (Gerlach et al. 2004; Guenther et al. 2007a, 2007b). It was concluded, that a hysteresis in the output characteristic of a pH sensor is caused by a hysteresis in the deprotonation-protonation process of ionizable groups in the gel as well as by a rather complicated hydrogel swelling and deswelling kinetics. It should be noted, that

- The previous states of both the gel ionization and the swelling influence the shape of the titration curve $c_{gi}=f(\text{pH})$. This means that high signal reproducibility can be ensured only by performing a conditioning procedure before every measurement in order to achieve a certain reference sensor signal.
- Even if the pH measurements are performed in buffered solutions of constant ionic strength, the formation of low molecular salt occurs in the gel at adjusting the pH value by adding acid or base for cycling from basic to acidic conditions and vice versa. As a result, the change of the ionic strength affects the value of the osmotic pressure and consequently the sign (positive or negative) of the resulting water flux.
- The dependence of the concentration of ionized groups (and consequently the water uptake) on the duration t_{ex} of the immersion in the solution leads to an additional dynamical hysteresis in the sensor output characteristic which can be minimized by setting constant t_{ex} for all pH measurements.

Fig. 6 (curves 2a and 2b) shows the sensor output characteristics obtained for repeated measurements at the same pH change direction and at the same value $U_{out,ref}$ of the reference sensor signal as well as at $t_{ex}=const$ for all pH measurements. In order to provide the required high signal reproducibility as well as in order to maintain a sufficient long-term stable sensitivity, three procedures have been carried out for the temperature sensitive gel:

- Initial gel conditioning procedure consisting of a gel swelling in de-ionized water and a subsequent deswelling/swelling cycling (see Sect. 2.4)
- Regenerating procedure before every measurement in order to achieve a certain reference sensor signal. This signal was gained by the gel deswelling at high temperature $T>T_{cr}$ (Fig. 10). The gel shrinking allowed to press out the previous measuring solution and to completely rinse the gel layer using a special rinsing solution (German Patent 2006). An additional rinsing cycle at $T<T_{cr}$ was carried out for those analytes which are particularly difficult to rinse out (Fig. 11). This complete cycle provides the full rinsing out of the previous solution from the gel and prevents its influence on the following measurement results. It should be

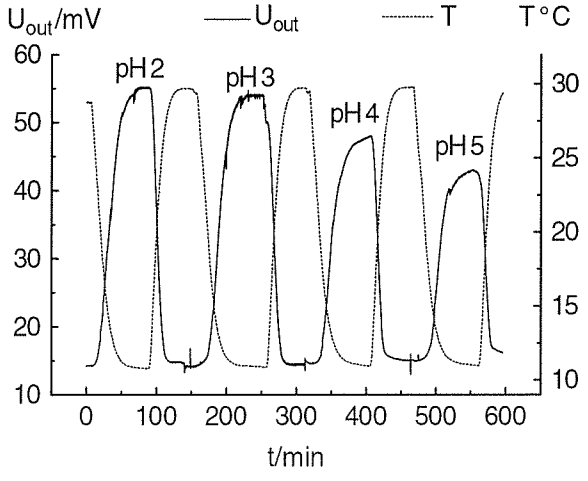


Fig. 10 Measuring and rinsing cycles for the temperature-sensitive P2VP-block-P(NIPAAm-co-DMIAAm) gel. Reprinted from (Guenther et al. 2007b) with kind permission from Elsevier

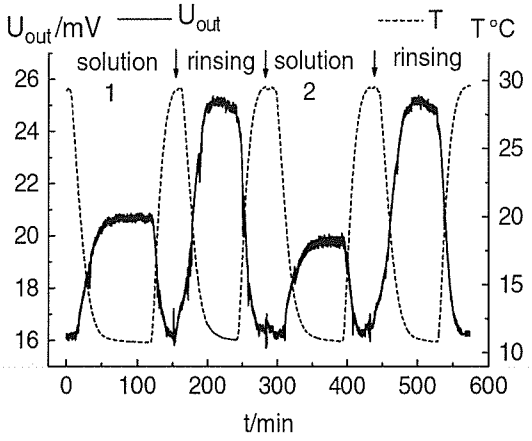


Fig. 11 Measuring cycle with additional gel swelling in rinsing solution at $T < T_{cr}$

noted that an appropriately chosen rinsing solution should be used for a certain analyte and for a certain polymer

- Rinsing in de-ionized water during sensor storage between measurements

A sufficiently long-term stable sensitivity during several working years of the pH sensors has been provided by performing these procedures as well as by avoiding large pH changes and measurements in solutions with pH < 2.

4 Sensors for Concentration Measurements in Aqueous Solutions

The swelling state of thermo-shrinking cross-linked polymers containing hydrophilic and hydrophobic groups depends on the balance of hydrophilic and hydrophobic interactions in the three-component system of polymer-water-analyte, which determine the polymer swelling/shrinking with changing temperature (Saito et al. 1993).The addition of a small amount of analyte to the water-swollen gel can perturb the water-polymer hydrogen bonding and therefore it can lead to a T_{cr}-shift.

Generally, the additives change the structure of water and thus the free energy of the interaction between polymer and water. The additives influence the solution viscosity and are classified into structure making (cosmotropes) and structure breaking (chaotropes). The viscosity η of an aqueous solution (up to about 0.1 M), relative to the viscosity η_0 of water at the same temperature, varies with the additive concentration c_α according to the Jones-Dole expression

$$\eta/\eta_0 = 1 + A\sqrt{c_\alpha} + Bc_\alpha, \tag{10}$$

where the coefficient A is related to the mobilities and interactions between the additives. The coefficient B reflects the interactions between the additive and the water molecules and results from the degree of water structuring. At higher

concentrations, a further term (Dc_α^2) may be added to the right hand side of Eq. (10) (Nickolov and Miller 2005). It has been accepted that the sign of the coefficient B determines whether a certain additive is a water structure breaker (negative B) or a water structure maker (positive B). Adding an analyte-cosmotrope as well as increasing the temperature leads to an enhancement of the polymer chain stiffness, which affects the chain mobility. In contrast, adding an analyte-chaotrope leads to the opposite effect.

A complex information containing the value of the swelling degree of the functionalised polymer in the presence of the additive, the value and direction of the induced T_{cr}-shift, and the value of the solution viscosity might allow to exactly detect the analyte as well as its concentration range. A portable biocompatible rheochemical microsystem for a comprehensive characterization of solutions, which combines a chemical sensor with a viscosity sensor and which could be embedded inside water systems for real time monitoring of organic and inorganic contaminants, is presented in (Guenther et al. 2008).

4.1 *Sensors for Organic Solvents*

In order to realize an organic solvent concentration sensor, we have used the ability of PNIPAAm to change its degree of swelling in water-organic solvent mixtures (Guenther et al. 2006, 2008). Fig. 12 demonstrates the output characteristic of such a sensor. The sensor's output voltage was measured during the swelling/shrinking of the hydrogel under the influence of water solutions with different ethanol contents at T=20 °C. Fig. 12 also shows the dependence of the relative viscosity η_{rel} of the ethanol-water mixture on the ethanol content c_α at T=20 °C. This dependence exhibits two flanks as well as the characteristic of the sensor with the PNIPAAm layer. The viscosity maximum is observed at about 40 vol.% of ethanol. The dependence $U_{out}=f(c_\alpha)$ demonstrates the broad asymmetric minimum corresponding to the shrunken state of the PNIPAAm hydrogel in the concentration range from 20 to 50 vol.% of ethanol. The shape of this characteristic is influenced

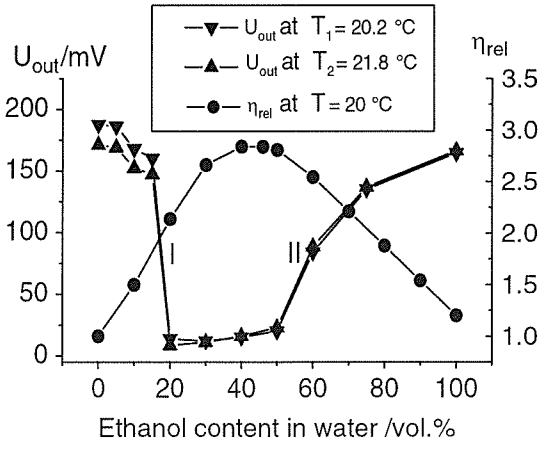


Fig. 12 Dependence of the output voltage U_{out} of a PNIPAAm (MBAAm 4)-based sensor and of the relative viscosity η_{rel} in aqueous ethanol mixtures on the ethanol content. Reprinted from (Guenther et al. 2006, 2008) with kind permission from SPIE and Elsevier

by the dependence of the partial molar volume of ethanol in aqueous solutions on the ethanol content, which runs through a sharp minimum at $c_\alpha < 30$ vol.% of ethanol (Hüther et al. 2004; Atkins 1990). The gel volume phase transition occurs at about 20 vol.% of ethanol. The first flank is induced by the shrinking of the hydrogel when the ethanol content is increased up to 40 vol.%. The second flank describes the hydrogel reswelling when the ethanol content is further increased from 50 to 100 vol.%. In order to exactly detect the ethanol concentration range, a small temperature rise was used. We have observed a gel shrinking at a small ethanol content (flank I) and a gel swelling at a high ethanol content (flank II) when we increased the temperature from $T=20.2$ °C to $T=21.8$ °C. With increasing temperature, the hydrophilic interactions dominating in the PNIPAAm-water-alcohol system at low alcohol content decrease leading to a hydrogel shrinking whereas the hydrophobic interactions dominating at high alcohol content increase and stimulate the gel swelling.

The polar organic additives of normal alcohols have a positive viscosity coefficient B and tend to enhance the hydrophobic interaction (for ethanol, $B=0.170$ l/mol) (Saito et al. 1993). The addition of a small amount of alcohol to the water-swollen gel perturbs the water-polymer hydrogen bonding and leads to strong polymer-polymer interactions. These are reflected as desorption of water by the gel, and shift the gel volume phase transition temperature T_{cr} to lower values. The T_{cr}-shift is stronger when the carbon number of alcohol is increased (Arndt et al. 2000; Saito et al. 1993; Kumar et al. 2006; Orakdogen and Okay 2006). At high alcohol concentration, when alcohol-polymer interactions overtake polymer-polymer interactions, the gel reswells. The competing weak interactions between organic solvent-water and organic solvent-polymer results in a complex "reentrant" swelling behavior of the hydrogel in mixed co-solvents.

A reswelling dynamics of PNIPAAm gel in mixed co-solvents was investigated at $T=20$ °C (Fig. 13). The water-swollen gel exhibits two successive states during reswelling in the solutions with an ethanol concentration higher than $c_\alpha^* = 50$ vol. %. Initially, the additive incoming into the gel has a lower concentration $c_{\alpha s1}$ in the gel subsurface layer than that one in the surrounding solution ($c_{\alpha s1} < c_\alpha^0$).

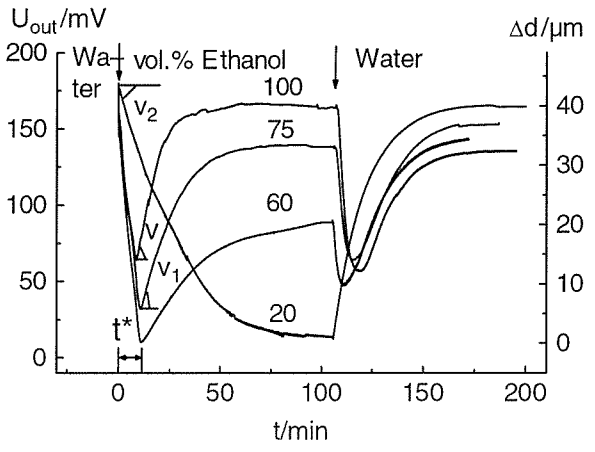


Fig. 13 Sensor output voltage U_{out} and change Δd of the gel layer thickness during the reswelling process of an initially water-swollen PNIPAAm (MBAAm 4) gel in solutions with different ethanol contents. Reprinted from (Guenther et al. 2008) with kind permission from Elsevier

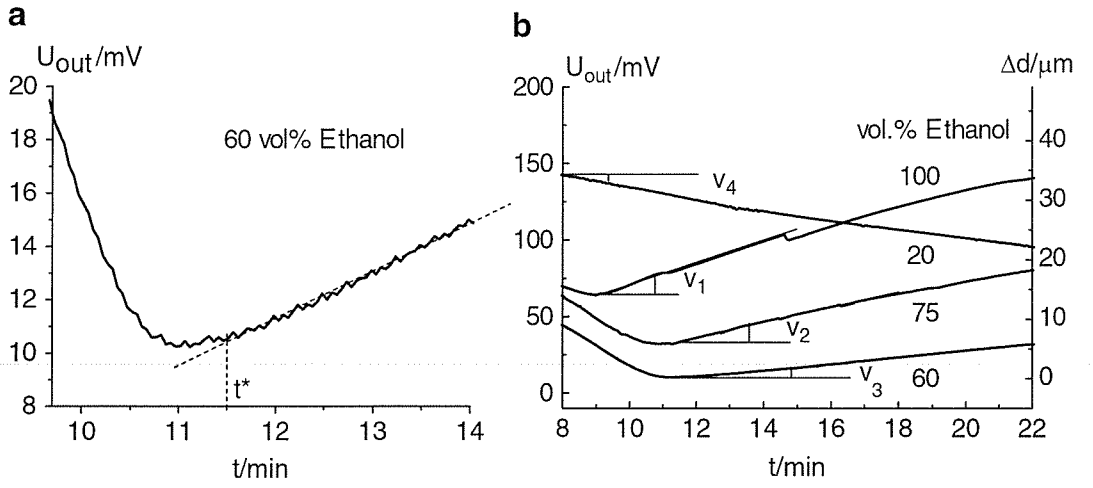


Fig. 14 Sensor output voltage U_{out} and change Δd of the gel layer thickness during the reswelling process of an initially water-swollen PNIPAAm (MBAAm 4) gel in solutions with different ethanol contents

This low additive concentration $c_{\alpha s1} < c_\alpha^*$ sparks off the gel collapse due to the suddently decreasing polymer-solution affinity. The interface between the outer collapsed and the inner swollen regions (shrinking front) proceeds from the outside towards the inside of the gel within the time $0 < t < t^*$. The change Δd of the gel layer thickness at small times $t \ll t^*$ is proportional to $t^{1/2}$. The concentration $c_{\alpha 1}$ increases with the time according to Eq. (6).

When the additive concentration $c_{\alpha 1}$ reaches the critical value of 50 vol.% at a depth $x = d$ (d is the thickness of the swollen gel layer), the gel begins to reswell (Fig. 14). At $t = t^*$ the boundary starts to move in the opposite direction. With the help of the values $t^* = 11.5$ min (see Fig. 14a), $c_\alpha^0 = 0.6$, $c_\alpha^* = 0.5$, and $d = 284$ μm the ethanol diffusion coefficient D_α in the swollen gel has been calculated using Eq. (6). The estimated value $D_\alpha = 1.3 \times 10^{-9}$ m^2 s^{-1} is in good agreement with the value $D_{MeOD} = 1.8 \times 10^{-9}$ m^2 s^{-1} obtained in (Arndt et al. 2006) for partially deuterated methanol in a D_2O-swollen PNIPAAm (MBAAm 4) hydrogel.

At $t > t^*$, the reswelling curve has an initial slope $v = \delta(\Delta d)/\delta t$ (Figs. 13 and 14b), which is determined by the rate of the ethanol sorption process and thereby is proportional to $(c_\alpha^0 - c_\alpha^*)$ as

$$v = k(c_\alpha^0 - c_\alpha^*). \tag{11}$$

Here, k is the rate constant. For an ethanol solution with a concentration $c_{\alpha,1}^0$, one obtains using Eq. (11)

$$v_1 = k(c_{\alpha,1}^0 - c_\alpha^*) = v(c_{\alpha,1}^0 - c_\alpha^*)/(c_\alpha^0 - c_\alpha^*). \tag{12}$$

Table 6 Values of the initial slope v of the hydrogel reswelling/shrinking curves and corresponding calculated values of the ethanol concentration c_α^0 of the investigated solutions. Reprinted from (Guenther et al. 2008) with kind permission from Elsevier

Solution	v, μm/min	c_α^0, vol.%
1	1.6	100
2	0.84	76
3	0.31	60
4	0.62	19.5

With the help of the values v and v_1 for two ethanol solutions with a known concentration $c_\alpha^0 > c_\alpha^*$ and with an unknown one $c_{\alpha,1}^0 > c_\alpha^*$, the value of $c_{\alpha,1}^0$ can be estimated as

$$c_{\alpha,1}^0 = c_\alpha^* + (c_\alpha^0 - c_\alpha^*)v_1/v. \tag{13}$$

For an ethanol solution with a small concentration $c_{\alpha,2}^0 < c_\alpha^*$, one uses

$$c_{\alpha,2}^0 = -(c_\alpha^0 - c_\alpha^*)v_2/v, \tag{14}$$

where $v_2 < 0$ is the initial slope at $t > 0$ for the second solution. Table 6 summarizes the values of the solution concentrations obtained from the slopes of the kinetic curves using the known value $c_\alpha^0 = 100$ vol.%. The calculated values of c_α^0 are in good agreement with the experimental values given in Figs. 13 and 14b. The same two-step reswelling kinetics is observed for an ethanol-swollen gel in water.

4.2 *Sensors for Salt Concentrations*

The chemical sensors based on cationic P2VP-block-P(NIPAAm-co-DMIAAm) gel as well as those based on neutral PNIPAAm and PNIPAAm-DMAAm-DMIAAm gels have demonstrated a clear dependence of the gel swelling degree on the salt concentration in aqueous solutions. Fig. 15a shows the value of the sensor signal at different concentrations of NaCl and NaI salts at $T = 20$ °C. The sensor characteristics demonstrate a "salting out" effect of NaCl salt in a PNIPAAm gel over the whole range of the salt concentration. In contrast, NaI shows a "salting in" effect at low concentrations in accordance with the hydration degree of Cl^- and I^- anions and their position in the Hoffmeister series. The strongly hydrated Cl^- ions exhibit strong interactions with water molecules, destroy the water-polymer hydrogen bonding and lead in this way to an enhancement of the gel hydrophobicity. Additionally, they shift the gel volume phase transition temperature T_{cr} to lower values proportionally to the increasing salt concentration (Figs. 15b and 16). The values of T_{cr} were determined as inflection points of the resulting sensor signal curves which are depicted versus the temperature. On the other hand, the I^- ions

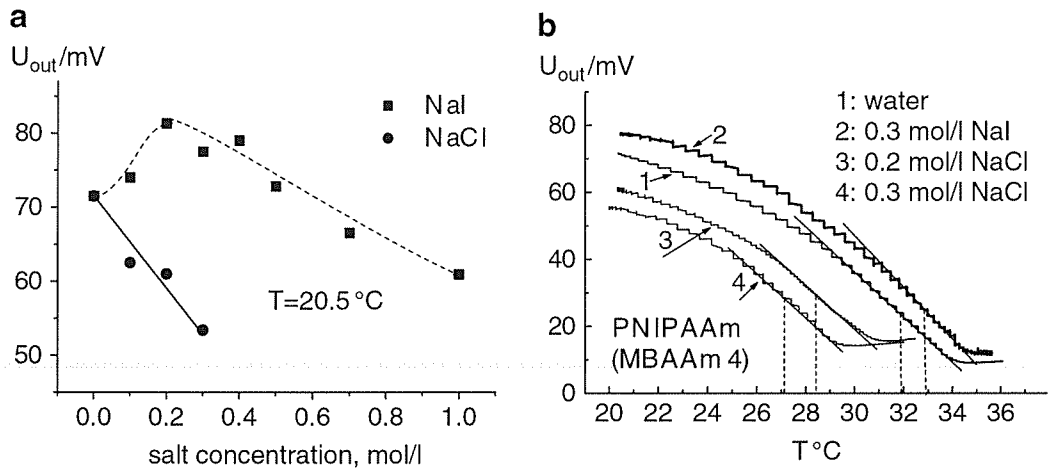


Fig. 15 Sensor signal (a) and its temperature dependence (b) for PNIPAAm (MBAAm 4) at different concentrations of NaCl and NaI salts. Reprinted from (Guenther et al. 2006, 2007b) with kind permission from SPIE and Elsevier

Fig.16 Gel volume phase transition temperature T_{cr} in solutions with different content of salts and metal ions. Reprinted from (Guenther et al. 2007b) with kind permission from Elsevier

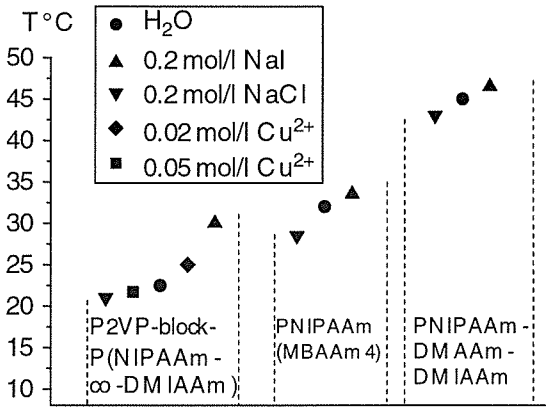


exhibit a weak hydration ability in water, tend to disperse the polymer chains, preventing them from intramolecular interactions, and as a result, increase the gel solubility at low NaI concentrations below 0.5 mol/l. The "salting in" effect of NaI salt in the PNIPAAm gel leads to a T_{cr}-shift to higher values (Figs. 15b and 16).

It should be noted that strongly hydrated salts increase the solution viscosity due to their tightly bound high-density ordered water and are known as water structure makers. The Cl^- ions have a viscosity coefficient B=-0.007 l/mol whereas I^- ions have a more negative B=-0.069 l/mol (Saito et al. 1993). They are known as water structure breakers and decrease the solution viscosity. Fig. 17 demonstrates the change of the sensor output voltage which corresponds to a change in the gel swelling degree in dependence on the relative viscosity of the 0.2 mol/l NaI and NaCl solutions for P2VP-block-P(NIPAAm-co-DMIAAm), PNIPAAm (MBAAm 4), and PNIPAAm-DMAAm-DMIAAm based sensors. The value of ΔU_{out} was calculated as the difference between the sensor signals obtained from a salt solution and from pure water. Adding NaCl salt as well as increasing the temperature leads to an enhancement of the polymer chain stiffness, which affects the chain mobility,

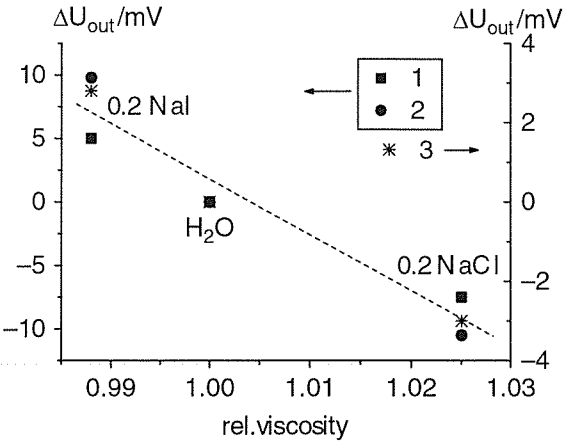


Fig. 17 Change of the sensor output voltage ΔU_{out} in dependence on the relative viscosity of the 0.2 mol/l NaI and NaCl solutions for P2VP-block-P(NIPAAm-co-DMIAAm) (1), PNIPAAm (MBAAm 4) (2), and PNIPAAm-DMAAm-DMIAAm (3) based sensors. Reprinted from (Guenther et al. 2007b) with kind permission from Elsevier

whereas adding NaI salt leads to the opposite effect. Finally, we note that multiresponsive hydrogels are very useful as sensitive material for measuring the rheochemical characteristics of solutions.

4.3 Sensors for Metal Ions Concentrations

The swelling behaviour of the P2VP-block-P(NIPAAm-co-DMIAAm) and PDMAEMA-DMIMA gels was analyzed as a function of the concentration C_{Me2+} of transition-metal ions in aqueous solutions. The dependence demonstrates a non-monotonic behaviour (Fig. 18). Since both P2VP-block-P(NIPAAm-co-DMIAAm) and PDMAEMA-DMIMA are weak polyelectrolytes (due to the amino groups), their uncompensated backbone charge increases at small ion concentrations. This leads to an increase of the gel hydrophilicity and consequently to a gel swelling at $c_{Me2+} < 0.03$ mol/l. A small change in the affinity of the comonomer with regard to the solvent has a large effect on swelling by shifting the phase transition temperature T_{cr} to higher values (Fig. 16).

With further increase of c_{Me2+}, more and more metal ions become trapped within the P2VP-block-P(NIPAAm-co-DMIAAm) and PDMAEMA-DMIMA gels which possess specific coordination binding sites for metal ions. The transition-metal cations form complexes with N atoms which have a pair of unshared electrons and are capable to satisfy the coordination number of the metal (Kuckling and Pareek 2003). As a result, the electrostatic repulsion between the charged units decreases, and the gel starts to contract. In this case, the metal ions might act as crosslinkers by coordination binding to nitrogen atoms of different chains. It was found that the complexation of the polymer units by divalent metal ions (due to the formation of chelate rings with metal ions) affects the T_{cr}-shifting toward lower values (Fig. 16) and increases in accordance with a series: $Ca^{2+} < Fe^{2+} < Cu^{2+} < Zn^{2+} < Mn^{2+} < Ni^{2+}$ (Fig. 18a).

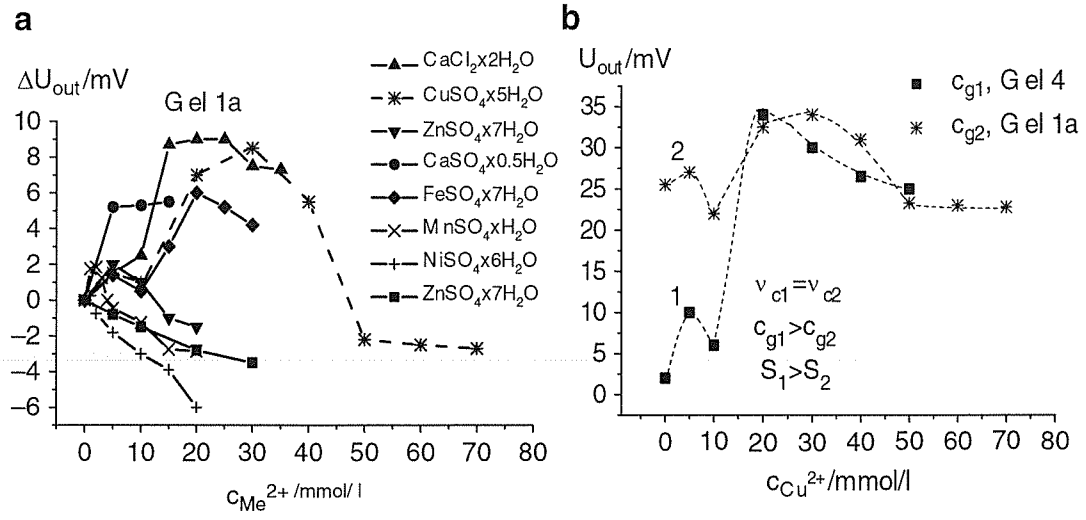


Fig. 18 Sensor output characteristics in solutions with transition-metal ions for (a) P2VP-block-P (NIPAAm-co-DMIAAm) (Gel 1a) and for (b) PDMAEMA-DMIMA (Gel 4) based sensors. Reprinted from (Guenther et al. 2007b, 2007c) with kind permission from Elsevier and Wiley-VCH

An increasing ionic strength I of the solution at $c_\alpha > 0.03$ mol/l is an additional reason for a decreasing equilibrium swelling. It results from the screening effect of the counter ions, i.e. SO_4^{2-}, which shield the charges on the polymer chains and prevent their efficient repulsion. Fig. 18b (curves 1 and 2) shows the sensor output characteristics obtained for two sensors with hydrogel layers of nearly the same cross-linking degree (i.e. nearly the same content of the cross-linking agent in the polymer and the same irradiation time) but with different concentrations c_g of ionizable groups ($c_{g1} > c_{g2}$) in the gels 4 and 1a (Table 2). One observes that the sensitivity S_1 is higher than S_2.

In order to provide the required high signal reproducibility of the sensors, a regenerating procedure before every measurement was carried out in order to achieve a certain reference sensor signal. An appropriate rinsing solution was chosen for a certain combination of analyte and polymer. A mixture of the phosphate buffer saline (PBS, 10 mg/ml) yielding pH=7.3 and 0.01 mol/l EDTA was found as a suitable rinsing solution for the P2VP-block-P(NIPAAm-co-DMIAAm) gel after measurements in solutions with metal ions.

Additionally, it should be noted that the pH value of the solution has a significant influence on the binding capacity of metal ions to amino groups. At low pH values, the metal ions cannot strongly affect the phase transition temperature of the gel. This is due to the protonation of the amino groups, which disrupts the interaction with metal ions (Oktar et al. 2005; Kuckling and Pareek 2003; Wang and Wang 2006; Chang et al. 2006). The absorption capacity of the hydrogels is important for the detection of metal ions in biological systems and for environmental monitoring of heavy metal ions. The functionalised hydrogels are widely used as chelating agents, as sorbents in such technical processes as electroplating, removal of toxic metal ions from waste-water, purification of sewage and drinking water.

5 Summary

We have demonstrated the operational principle of hydrogel-based piezoresistive chemical sensors. In order to realize chemical sensors, the polyelectrolyte as well as neutral gels were used as chemo-mechanical transducers. The hydrogel swelling leads to a bending of a thin silicon plate and, by this, to an electrical output voltage of the sensor chip. Combining a hydrogel and a micro fabricated pressure sensor chip allowed to continuously monitor the analyte-dependent swelling of a hydrogel in aqueous solutions. The sensitivity of hydrogels with regard to the concentration of such additives as H^+-ions (pH sensor), transition-metal ions, salts and organic compounds in water was investigated. It has been demonstrated that the sensitivity depends on the polymer composition as well as on the polymer cross-linking degree. A higher sensitivity was observed for polyelectrolyte hydrogels with higher concentrations of ionizable groups.

Changes in the composition of thermo-shrinking *N*-isopropylacrylamide (NIPAAm) copolymer gels have allowed to vary the gel *volume phase transition temperature* (T_{cr}) from 22 °C for P4VP-block-P (NIPAAm-co-DMIAAm) to 43 °C for PNIPAAm-DMIAAm-DMAAm terpolymer. This possibility for variations of the working temperature range is particularly relevant with respect to possible applications of the chemical sensors. It was shown that the phase transition of the gel is influenced by the ion concentration in aqueous solutions as well as by the viscosity of the solution. By this, we have demonstrated that multiresponsive smart hydrogels are promising materials for a rheochemical characterization of solutions.

Because the gel response is typically diffusion-driven, the time response of the volume change approximately follows the square of the sample dimension. Scaling to micro-dimensions enhances the time response. Consequently, a reduction of the sample size improves the sensor performance. Time constants down to a few ten seconds have been found for thin hydrogel films deposited directly on the backside of the silicon bending plate. In order to achieve an optimum between sensor signal amplitude and sensor response time, the gel swelling/deswelling kinetics was investigated. It was found that the sensor response time and signal reproducibility is limited by the visco-elastic and hysteresis behaviour of the polymer material. Some methods improving the properties of the chemical sensors have been proposed. An analysis of the measured swelling/deswelling kinetic curves by means of appropriate models allowed to essentially shorten the measuring time which is necessary to determine the additive concentration in a solution.

Beside sensitivity and response time, signal reproducibility and long-term stability are the most crucial aspects for a successful sensor implementation. Since the sensor chips show excellent stable properties, the long-term stability of the sensor is solely determined by the stability of the hydrogel characteristics. The polymer film preparation conditions and measurement conditions, which are necessary for high signal reproducibility and high long-term stable sensor sensitivity, were determined. In order to provide the required high signal reproducibility of the sensors, two

procedures were carried out: (1) an initial gel conditioning procedure consisting of a gel swelling in de-ionized water and a subsequent deswelling/swelling cycling, and (2) a regenerating procedure before every measurement in order to achieve a certain reference sensor signal. The long-term measurements have shown that the life time of piezoresistive chemical sensors can be prolonged up to several years provided that specific operation and storage conditions are fulfilled.

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