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Polyaniline Nanoparticle-Based Solid-Contact Silicone Rubber Ion-Selective Electrodes for Ultratrace Measurements

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Silicone rubber (SR)-based solid-contact ion-selective electrodes (ISEs) have been prepared for the first time with an electrically conducting polymer as the solid-contact (SC) layer. The Ca^{2+}- and Ag^+-selective electrodes were based on the ionophores ETH 1001 and *o*-xylylenebis(*N,N*-diisobutyl dithiocarbamate), respectively, integrated in room temperature vulcanizing silicone rubber (RTV 3140). The SC consisted of a polyaniline nanoparticle dispersion, which was found to considerably lower the impedance of the SCISEs in comparison to the SR-based coated wire electrodes (CWE). For the CaSCISEs, the bulk membrane resistance decreased from 700 MΩ (CaCWE) to 35 MΩ. Both the Ca^{2+}- and Ag^+-selective SCISEs exhibited nanomolar detection limits with fast Nernstian responses down to 10^{-8} M. The potential response of the SCISEs was not influenced by light. The selectivities of the CaSCISEs were similar and for the AgSCISE better than their plasticized PVC-based analogues. Thus, SR seems to be a viable alternative to PVC membranes in ISE applications that require low water uptake, good adhesion, and robust and fast potential responses at submicromolar sample concentrations.

Plasticized poly(vinyl chloride) (PVC) is the most commonly used membrane matrix for potentiometric ion-selective electrodes (ISEs) due to its good compatibility with ionophores, easy handling, and chemical inertness.[1] On the downside, slow leaching of plasticizers and ionophores from the PVC membrane,[2] its limited adhesion to a number of supporting materials, extraction of selectivity altering lipophilic compounds from biological samples,[3] and its high water uptake[4] and ion mobility[5−7] were found restrictive for some applications. The search for alternative membrane materials was therefore motivated by the need to overcome one or more of the above-mentioned shortcomings.[2,8] Recently, the importance of substituting PVC membranes gained additional attention with the introduction of mass-transport-controlled ISEs[9] and their applications for trace analysis.[10] These electrodes are based on eliminating, usually by an applied chemical gradient[9,11] or electrical current,[12−15] the primary ion leaching from the ion-selective membranes (ISMs), which by contaminating the sample solution at the ISM/solution interface worsen the attainable limit of detection (LOD).[16] Such ion fluxes, induced by the nonideal permselectivity and selectivity of ISMs, are also greatly suppressed by simply using membranes with low ion diffusion rates.[17] Therefore, different types of poly(acrylate) (PA) membranes[8] with approximately 3 orders of magnitude lower ion diffusion rates ($\sim 10^{-11}$ cm^2 s^{-1})[18] than that of plasticized PVC got established as probably the best candidates for preparing low detection limit ISEs.

The focus of ISE research during recent years, however, has been redirected from liquid contact ISEs toward solid-

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(1) Bakker, E.; Buhlmann, P.; Pretsch, E. *Chem. Rev.* **1997**, *97*, 3083–3132.
(2) Reinhoudt, D. N.; Engbersen, J. F. J.; Brzozka, Z.; Vandenvlekkert, H. H.; Honig, G. W. N.; Holterman, H. A. J.; Verkerk, U. H. *Anal. Chem.* **1994**, *66*, 3618–3623.
(3) Buhlmann, P.; Hayakawa, M.; Ohshiro, T.; Amemiya, S.; Umezawa, Y. *Anal. Chem.* **2001**, *73*, 3199–3205.
(4) Lindfors, T.; Sundfors, F.; Höfler, L.; Gyurcsányi, R. E. *Electroanalysis* **2009**, *21*, 1914–1922.
(5) Zook, J. M.; Bodor, S.; Gyurcsányi, R. E.; Lindner, E. *J. Electroanal. Chem.* **2010**, *638*, 254–261.
(6) Zook, J. M.; Bodor, S.; Lindner, E.; Tóth, K.; Gyurcsányi, R. E. *Electroanalysis* **2009**, *21*, 1923–1930.
(7) Bodor, S.; Zook, J. M.; Lindner, E.; Tóth, K.; Gyurcsányi, R. E. *Analyst* **2008**, *133*, 635–642.
(8) Heng, L. Y.; Hall, E. A. H. *Anal. Chim. Acta* **1996**, *324*, 47–56.
(9) Sokalski, T.; Ceresa, A.; Zwickl, T.; Pretsch, E. *J. Am. Chem. Soc.* **1997**, *119*, 11347–11348.
(10) Ceresa, A.; Bakker, E.; Hattendorf, B.; Gunther, D.; Pretsch, E. *Anal. Chem.* **2001**, *73*, 343–351.
(11) Ceresa, A.; Sokalski, T.; Pretsch, E. *J. Electroanal. Chem.* **2001**, *501*, 70–76.
(12) Pergel, E.; Gyurcsányi, R. E.; Tóth, K.; Lindner, E. *Anal. Chem.* **2001**, *73*, 4249–4253.
(13) Lindner, E.; Gyurcsányi, R. E.; Buck, R. P. *Electroanalysis* **1999**, *11*, 695–702.
(14) Höfler, L.; Bedlechowicz, I.; Vigassy, T.; Gyurcsányi, R. E.; Bakker, E.; Pretsch, E. *Anal. Chem.* **2009**, *81*, 3592–3599.
(15) Bedlechowicz, I.; Sokalski, T.; Lewenstam, A.; Maj-zurawska, M. *Sens. Actuators, B:* **2005**, *B108*, 836–839.
(16) Gyurcsányi, R. E.; Pergel, E.; Nagy, R.; Kapui, I.; Lan, B. T. T.; Tóth, K.; Bitter, I.; Lindner, E. *Anal. Chem.* **2001**, *73*, 2104–2111.
(17) Vigassy, T.; Gyurcsanyi, R. E.; Pretsch, E. *Electroanalysis* **2003**, *15*, 375–382.
(18) Heng, L. Y.; Tóth, K.; Hall, E. A. H. *Talanta* **2004**, *63*, 73–87.

contact ion-selective electrodes (SCISEs) with electrically conducting polymers (CP) as one of the most established solid-contact (SC) materials. It has been shown that the elimination of the liquid contact, which sustains the primary ion leaching from the membrane, together with proper conditioning of the ISMs leads to SCISEs with low LOD.[19] In this respect, however, it is especially important to use membranes characterized by low ion diffusion rates, as they provide stable potentials at low primary ion concentrations. Accordingly, the detection limit of SCISEs could be significantly decreased by using PA-based membranes instead of PVC.[20] Thus SCISEs, which in addition are inherently easier to miniaturize[21,22] and are compatible with microfabrication technologies,[23] provide probably the most straightforward route to construct ISEs for trace analysis.

Besides the rate of ion transport, the water uptake of ISMs is also important with respect to the attainable LOD and potential stability.[24] It was postulated that a higher water uptake of the ISM results in a higher accumulation (concentration) of primary ions in the membrane phase, which may leach out from the ISM to contaminate the ISM/solution interface prohibiting measurements at low sample concentrations. Moreover, in the case of SCISEs, the water uptake of the ISMs can lead to the formation of an aqueous layer or scattered islands of water at the substrate/SC and/or the SC/ISM interface,[25] as well as to a decreased adhesion of the membrane to the SC. These processes have adverse effects both on the potential stability and the LOD of the respective SCISEs.[24]

Until recently, it was believed that the water uptake of PA membranes was lower than for their plasticized PVC counterparts. This is probably true on short time scales due to the lower diffusion coefficients in PA membranes, but it has been shown with FTIR-ATR measurements that the equilibrium water uptake is in fact much higher for different PA membranes than for plasticized PVC.[26] We have recently shown by FTIR-ATR spectroscopy that the water uptake of ISMs based on low temperature vulcanizing silicone rubber (SR), commercialized as an insulating coating in the electrical industry, is much lower than that of plasticized PVC and PA membranes. In addition, SRs usually have a superior adhesion[27] to different substrates in combination with good mechanical properties and is associated with lower nonspecific adsorption of proteins in biological samples. While the use of SRs as a membrane matrix for ISEs was reported already in 1973,[28,29] since then, various SR-based ISEs have been studied only to a minor extent and for a limited range of ions: Na$^+$,[30−32]

K$^+$,[31,33−35] H$_3$O$^+$,[31,33,34] NH$_4^+$,[34,35] Ca^{2+},[31,33,34,36] and CO$_3^{2-}$.[33] The limited use of SRs is mainly explained by the poor solubility of ionophores in most of the SRs and the high bulk impedance of SR-based ISEs.

In this work, we have made use of the low water uptake of the SR membranes[26] and the good stability of the electrically conducting form of a polyaniline nanodispersion (PANI (D1003))[37] to prepare Ca^{2+}- and Ag$^+$-selective SR-based SCISEs (CaSCISEs and AgSCISEs). Apart from conventional PANI materials, we have previously found that the electrically conducting emeraldine salt (ES) form of PANI (D1003) has excellent pH stability at pH ≤ 10.

To the best of our knowledge, this is the first report on SR-based SCISEs with an electrically CP as the ion-to-electron transduction layer as well as the first attempt to assess the feasibility of using SR membranes for constructing low LOD ion-selective electrodes.

EXPERIMENTAL SECTION

Chemicals. Room temperature vulcanizing silicone rubber (RTV 3140) was obtained from Dow Corning. Bis(2-ethylhexyl) sebacate (DOS), potassium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (KTFPB), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (NaTFPB), calcium ionophore I (ETH 1001), copper(II) ionophore I (o-xylylenebis(N,N-diisobutyl dithiocarbamate)); and tetrahydrofuran (THF) of Selectophore grade were received from Fluka. The polyaniline dispersion (PANI(D1003)) was obtained from Ormecon GmbH (Cookson Electronics) and had a mean particle size of 8 nm. The size of 90% of the particles was <14 nm, and the conductivity in vacuum was given as 1.8×10^{-3} S/cm. The dispersion had a solid content of 9.7 wt % and was stored in a closed glass bottle. The average molecular weight of the PANI dispersion is not provided by the manufacturer and cannot be reported.

Preparation of the CaCWEs and CaSCISEs. The SR-based CaSCISEs, AgSCISEs, and the calcium- and silver-coated wire electrodes (CaCWEs and AgCWEs; without a SC layer) were prepared by drop casting. The SC layers were usually prepared by applying 3 μL of PANI on GC or Au electrodes (polyether ether ketone (PEEK) body). The SC layers were allowed to dry overnight before 25 μL of the outer SR-based Ca^{2+}- or Ag$^+$-selective membrane solution (dry weight: 31%) was applied on the top of the SC layer. The SR membrane solution was prepared with a rather high viscosity to minimize excess THF that could dissolve the PANI solid contact, which is soluble in

(19) Sutter, J.; Lindner, E.; Gyurcsanyi, R. E.; Pretsch, E. *Anal. Bioanal.Chem.* **2004**, *380*, 7–14.
(20) Sutter, J.; Radu, A.; Peper, S.; Bakker, E.; Pretsch, E. *Anal. Chim. Acta* **2004**, *523*, 53–59.
(21) Sundfors, F.; Bereczki, R.; Bobacka, J.; Tóth, K.; Ivaska, A.; Gyurcsányi, R. E. *Electroanalysis* **2006**, *18*, 1372–1378.
(22) Gyurcsányi, R. E.; Nyback, A. S.; Tóth, K.; Nagy, G.; Ivaska, A. *Analyst* **1998**, *123*, 1339–1344.
(23) Gyurcsányi, R. E.; Rangisetty, N.; Clifton, S.; Pendley, B. D.; Lindner, E. *Talanta* **2004**, *63*, 89–99.
(24) Fibbioli, M.; Morf, W. E.; Badertscher, M.; de Rooij, N. F.; Pretsch, E. *Electroanalysis* **2000**, *12*, 1286–1292.
(25) Veder, J.-P.; De Marco, R.; Clarke, G.; Chester, R.; Nelson, A.; Prince, K.; Pretsch, E.; Bakker, E. *Anal. Chem.* **2008**, *80*, 6731–6740.
(26) Sundfors, F.; Lindfors, T.; Höfler, L.; Gyurcsányi, R. E. *Anal. Chem.* **2009**, *81*, 5925–5934.
(27) Anker, P.; Wieland, E.; Ammann, D.; Dohner, R. E.; Asper, R.; Simon, W. *Anal. Chem.* **1981**, *53*, 1970–1974.

(28) Pick, J.; Pungor, E.; Vasak, M.; Simon, W. *Anal. Chim. Acta* **1973**, *64*, 477–480.
(29) Fiedler, U.; Ruzicka, J. *Anal. Chim. Acta* **1973**, *67*, 179–193.
(30) Poplawski, M. E.; Brown, R. B.; Rho, K. L.; Yun, S. Y.; Lee, H. J.; Cha, G. S.; Paeng, K.-J. *Anal. Chim. Acta* **1997**, *355*, 249–257.
(31) Malinowska, E.; Oklejas, V.; Hower, R. W.; Brown, R. B.; Meyerhoff, M. E. *Sens. Actuators, B* **1996**, *33*, 161–167.
(32) Kimura, K.; Matsuba, T.; Tsujimura, Y.; Yokoyama, M. *Anal. Chem.* **1992**, *64*, 2508–2511.
(33) Yoon, I. J.; Lee, D. K.; Nam, H.; Cha, G. S.; Strong, T. D.; Brown, R. B. *J. Electroanal. Chem.* **1999**, *464*, 135–142.
(34) Mostert, I. A.; Anker, P.; Jenny, H. B.; Oesch, U.; Morf, W. E.; Ammann, D.; Simon, W. *Mikrochim. Acta* **1985**, *1*, 33–38.
(35) Cha, G. S.; Liu, D.; Meyerhoff, M. E.; Cantor, H. C.; Midgley, A. R.; Goldberg, H. D.; Brown, R. B. *Anal. Chem.* **1991**, *63*, 1666–1672.
(36) Marrazza, G.; Mascini, M. *Electroanalysis* **1992**, *4*, 41–43.
(37) Lindfors, T.; Aarnio, H.; Ivaska, A. *Anal. Chem.* **2007**, *79*, 8571–8577.
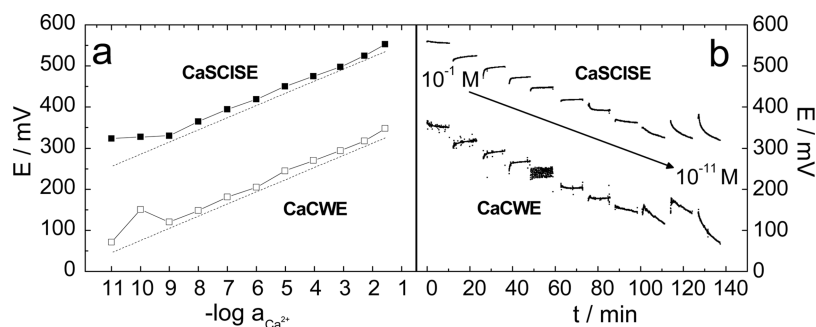
Figure 1. Calibration curves of an unconditioned CaSCISE and CaCWE (a) and their corresponding potential traces (b). The theoretical responses (25 °C) are denoted with the dashed lines.

THF. The CaCWEs and AgCWEs were prepared in the same way but without the SC intermediate layer. The SCISEs and the CWEs were then allowed to dry overnight. Note, after weighing in the SR, it was dissolved immediately in THF in order to avoid the premature start of the curing as it comes in contact with atmospheric humidity. The SR-based ISM was composed either of (i) 98.1 wt % SR (RTV 3140), 1.0 wt % (14.6 mmol/kg) calcium ionophore I and 0.9 wt % (10.0 mmol/kg) KTFPB (CaISEs),[31] or (ii) 88.55 wt % SR, 0.8 wt % (17.1 mmol/kg) o-xylylenebis(N,N-diisobutyl dithiocarbamate), 0.65 wt % (6.8 mmol/kg) NaTFPB, and 10 wt % DOS as plasticizer to facilitate the solubilization of the silver ionophore (AgSCISEs).

For the PVC-based AgISEs and AgCWEs, the membrane cocktails (dry weight: 31%) consisting of 0.87 wt % (17.1 mmol/kg) copper(II) ionophore I, 0.63 wt % (6.9 mmol/kg) NaTFPB, 55.45 wt % DOS, and 43.05 wt% PVC were deposited similarly as described for the SR membranes and allowed to dry for 2−3 h.

Potentiometric Measurements. The CaISEs were conditioned overnight in a 1 mM $CaCl_2$ solution unless otherwise mentioned. Before starting the calibrations, the electrodes were placed in a stirred 0.1 M NaCl solution for ~1 h and then transferred to a stirred solution of deionized water for 1−4 h. The AgISEs were conditioned in stirred 1 mM $AgNO_3$ solution for 2 days and then in 10^{-9} M $AgNO_3$ for 1 day. The solutions below 10^{-5} M were always prepared freshly just before the calibration in hydrophobic polypropylene beakers of 500 mL (or 100 mL Teflon beakers) that had been fully equilibrated with the respective ion. One beaker was dedicated for one specific ion concentration, and the solution was remade in the same beaker by weighing before each measurement. In this way the use of volumetric flasks, transfer pipettes, and any volumetric glassware that have been shown to adsorb or release ions was avoided.

The potential response curves were recorded in stirred solutions with a 16-channel high impedance (10^{15} Ω) voltmeter (Lawson Laboratories Inc., Malvern, PA). A double junction Ag|AgCl reference electrode (RE) with 3 M KCl and 1.0 M KCl in the inner and outer compartments, respectively, was used for the Ca^{2+}-measurements while for the Ag^+-measurements, the outer compartment was filled with 1 M KNO_3. Unbiased selectivity coefficients were determined with ISMs, which had not previously been in contact with their primary ions. The separate solution method at 0.1 M level was used for the CaISEs, while for the AgISEs, the selectivity coefficients were calculated by using the individual potentials extrapolated to an activity of 1 based on a 2-point calibration at 10^{-3} and 10^{-4} M levels in the nitrate salt solutions of the primary Ag^+ ions (I) and interfering cations (J).

Impedance Measurements. All impedance spectra in this work were measured within the frequency range of 100 kHz to 10 mHz in 1 mM $CaCl_2$ (CaISEs) or 1 mM $AgNO_3$ (AgISEs) solutions by using an Autolab PGSTAT 12 potentiostat/galvanostat equipped with a FRA2 impedance module. The excitation potential (ΔE_{ac}) was 100 mV unless otherwise mentioned.

RESULTS AND DISCUSSION

Potentiometric Response and Selectivity of SR-Based ISEs. In general, if the SC provides proper potential stability at the inner membrane interface, the potentiometric selectivities and calibration properties are solely determined by the ISM.[38] We have however observed that the PANI layer was slightly dissolved in the outer Ca^{2+}-selective SR membrane during drop casting of the outer SR membrane, which is beneficial in obtaining good mechanical strength and adhesion of the SC/SR interface.[37] On the other hand, it is necessary to determine how this intermixing affects the potential response of the CaSCISE. Therefore, the performance of the CaSCISEs and CaCWEs were assessed side-by-side during the calibration and selectivity determinations. First, the electrodes were calibrated in $10^{-1}-10^{-11}$ M $CaCl_2$ solutions under continuous stirring (Figure 1). Both the CaSCISE and the CaCWE (membrane thicknesses: ~200−250 μm) provided close to Nernstian slopes (Table 1). The potential traces of the CaSCISE showed that the potentials in $CaCl_2$ solutions with concentrations $>10^{-7}$ M stabilize within ca. 3 min to a value ≤1 mV of the potentials measured after a contact time of 10 min. However, the response time became considerably longer at concentrations $<10^{-7}$ M. As shown in Figure 1b, the main benefit of the PANI nanoparticle-based SC is obviously the reduced potential noise.

The much noisier potential of the CaCWE associated with standard deviations up to 8.4 mV in the investigated concentration range is due to the high resistance of the electrode membrane (see Impedance Measurements). Taking the stirring effect into account, the almost noiseless potentials of the CaSCISEs are due to the efficiency of the electrically conducting PANI-based SC to function as an ion-to-electron transducer between the electronically conducting substrate and the ionically conducting SR membrane.

(38) Lindner, E.; Gyurcsányi, E. R. *J. Solid State Electrochem.* **2009**, *13*, 51−68.

Table 1. Slopes and Linear Ranges of the Potentiometric Calibration Curves of SR and Plasticized PVC-Based CWEs and SCISEs[a]

	slope (mV/decade)	concentration range (M)
SR		
CaCWE	28.3 (0.997)	10^{-1} to 10^{-8}
CaSCISE	30.6 (0.987)	10^{-1} to 10^{-8}
AgCWE	54.5 (0.998)	10^{-4} to 10^{-7}
		(supernernstian: 10^{-7} to 10^{-9})
AgSCISE	54.7 (0.999)	10^{-4} to 10^{-7}
PVC		
AgCWE	55.6 (1.000)	10^{-4} to 10^{-6}
		(supernernstian: 10^{-7} to 10^{-9})
AgSCISE	46.8 (0.984)	10^{-4} to 10^{-6}

[a] The value of r^2 is given in parentheses.

Also the slight dissolution of the PANI solid-contact layer into the upper SR-based CaISM (during drop casting of the SR membrane) is beneficial for lowering the noise of the CaSCISEs. The intermixing of PANI and the upper SR membrane considerably lowered the resistance of the CaSCISE in comparison to the CaCWE (see Impedance Measurements). The possible postdiffusion of PANI into the SR membrane, i.e., after the curing process, was studied by contacting a blank SR membrane (without PANI) with a SR membrane containing 2 wt % PANI. During 24 h, no changes were observed in the UV−vis spectrum of the contacted membranes, measured by spectroelectrochemical microscopy (SpECM)[39,40] over a cross-section of the interface between the two membranes. The membranes had cured for 24 h before the measurements. This indicates that neither PANI nanoparticles nor oligomeric fragments will diffuse from the PANI solid contact into the outer SR matrix. The minor intermixing of the SC and the SR membrane is therefore attributed to the slight redissolution of PANI in THF during the casting of the ISM cocktail (see also Experimental Section).

The LOD of both the CaSCISE and the CaCWE was ca. 10^{-9} M. It should be stressed, that the calibrations shown in Figure 1 were done from 0.1 M down to 10^{-11} M CaCl$_2$ with unconditioned electrodes. However, when the calibrations were done from low to high concentrations with unconditioned electrodes, they exhibited a supernernstian potential jump of ca. 220 mV between 10^{-8} M and 10^{-7} M CaCl$_2$ (data not shown). This so-called Hulanicki effect is due to the high uptake rate of primary ions by the ISM that ensures virtually zero concentration of Ca^{2+} in the solution layer in immediate contact with the ISM. The surface concentration increases only when the bulk concentration becomes high enough to establish mass transfer rates that exceed the rate of primary ion uptake by the membrane. The very low concentrations at which the supernernstian jump occurs suggest that the low diffusivity SR membranes will provide a much more robust potential response than their PVC-based analogues. It must be stressed that the purpose of the measurements with the CaSCISE and CaCWE shown in Figure 1 is to determine their initial response characteristics and not to suggest using the electrodes unconditioned. Since the new SCISE construction presented in this paper consists of a low diffusivity membrane in combination with a CP-based solid-contact material, which has been studied only to a minor extent, it is essential to investigate the response of the unconditioned electrodes and the time required to reach a steady-state response (Figure 2).

In order to demonstrate that potentiometric responses can be routinely and reproducible obtained at ultratrace concentration levels, three identically prepared CaSCISEs were conditioned for 24 h in 10^{-9} M CaCl$_2$ before the measurements. Figure 2 shows the potential traces and the corresponding calibration curves of the respective ISEs. The potentiometric slopes were 28.0 ± 0.5 mV/decade (10^{-5}–10^{-8} M) and 26.8 ± 0.5 mV/decade (10^{-5}–10^{-9} M). The potential response curves in Figure 2b show that the equilibrium is established rather fast at all Ca^{2+} concentrations and that the electrodes are responsive from 10^{-9} M (LOD = 2×10^{-9} M). Most remarkably, however, the CaSCISEs showed good reproducibility of the E^0 values, which has been proved to be a major challenge for most SCISEs. Note, similarly good reproducibility of the E^0 values was observed for uncoated PANI(D1003) membranes exhibiting a standard deviation of less than 3.8 mV within pH 0−12.

There is rather good agreement between the selectivity coefficients of CaSCISEs and CaCWEs, which indicates that the slight intermixing of the PANI nanoparticle dispersion and the ISM does not affect the selectivity of the CaSCISEs (Table 2). In fact, the selectivity coefficients of the CaSCISEs are even slightly better than for the CaCWEs. Since the measuring protocols (timing) were the same for both type of electrodes the small difference in the selectivities seems to be due to the slightly drifting potentials of the CaCWEs upon solution exchange, which in contrast to the stable potential response obtained immediately for the CaSCISEs affects the potential reading.

The values in parentheses for the CaSCISE are taken from Fluka (conventional composition PVC membranes with bis(1-
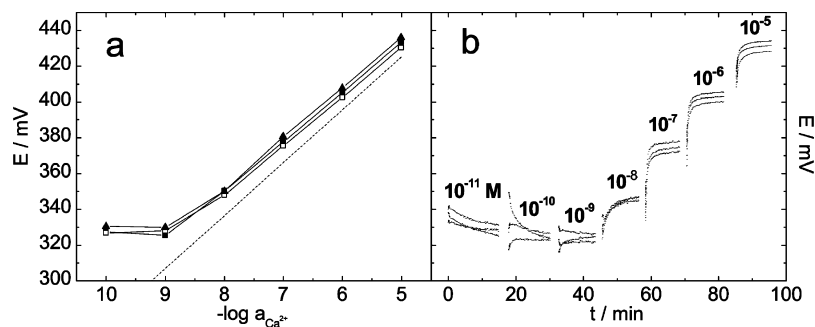

Figure 2. Calibration curves of three identically prepared CaSCISEs conditioned in 1 nM CaCl$_2$ for 24 h (a) and their corresponding potential traces (b). The theoretical responses (25 °C) are denoted with the dashed lines.

Table 2. Unbiased Selectivity Coefficients of the SR and Plasticized PVC-Based CWEs and SCISEs

	$\log K_{I,J}^{pot}$							
	SR (I = Ca^{2+})		SR (I = Ag$^+$)					PVC (I = Ag$^+$)
			AgCWE[a]		AgSCISE[a]		AgSCISE[b]	
J	CaCWE	CaSCISE	10% DOS	5% DOS	10% DOS	5% DOS	10% DOS	AgSCISE
Na$^+$	−2.5	−3.0 (−3.7)	−13.5	−14.9	−12.7	−12.8	−9.5	−10.4 (−11.5)
K$^+$	−2.6	−3.0 (−3.7)	−13.1	−14.6	−12.4	−12.8	−9.2	−6.5 (−7.7)
Mg^{2+}	−3.6	−3.8 (−4.7)	−15.5	−16.6	−12.8	−11.0	−11.1	−8.4 (−10.9)
H$^+$	−2.9	−3.1 (−2.9)	−12.2	−13.5	−13.0	−13.3	−8.6	−6.1 (−10.9)
Ca^{2+}	−	−	−15.1	−16.5	−13.2	−12.8	−10.9	−7.7 (−12.9)
Cu^{2+}	−	−	−12.6	13.9	−12.4	−12.6	−8.8	−9.7 (−8.2)

[a] Typical standard deviations for the selectivities were ≤0.2 units for the CaCWEs and CaSCISE, and 0.6 and 1.4 for the AgCWE and AgSCISE, respectively. [b] The Ag$^+$-selective membrane cocktail (25 μL) and the PANI nanoparticle dispersion (3 μL) were mixed before being applied in one step on the electrode surface.

butylpentyl)decan-1,10-diyl diglutarate as the plasticizer and liquid contact) while those for the AgSCISE are from ref 42 (oNPOE plasticised PVC membranes and liquid contact).

There is some controversy in the literature regarding the selectivity of ETH 1001-based membranes, as the selectivity coefficients depend very much on the membrane composition. For PVC membranes, the best results in terms of discrimination against alkali ions were obtained for o-nitrophenyl octyl ether (oNPOE) plasticized membranes with selectivity coefficients approaching 10^{-6}. However, these membranes exhibited extremely poor proton selectivity (log $K_{Ca,H} = −1.8$).[27] More lipophilic plasticizers, such as DOS, were found to improve the proton selectivity but in turn lowered the selectivity toward alkali metals. The selectivity of SR-based CaCWEs and CaSCISEs prepared in the present study are slightly lower than for DOS-plasticized PVC membranes, however, with a slightly better proton selectivity (log $K_{Ca,H}^{pot} = −3.1$ for CaSCISEs). Interestingly, a study on ETH 1001-based SR ISEs showed that the electrode had close to Nernstian slopes only when either tetradodecylammonium tetrakis(p-chlorophenyl) borate (ETH 500) or DOS was added into the membrane cocktail[41] while reasonable alkali ion selectivities required both components. The reason for the discrepancy with the present results is not completely clear; one major difference is that the authors used TpClPB$^-$ as cation-exchanger, which was found by Malinowska et al.[31] to lead to subnernstian responses as opposed to the more lipophilic and stable TFPB$^-$ used in the present study.

Since Ca^{2+}-selective electrodes exhibited significantly lower LOD than any previously reported SR-based electrodes, we were also interested to investigate the feasibility of extending the use of SR matrixes to other ions. We chose to study Ag$^+$-selective electrodes motivated by the fact that besides the divalent calcium, cadmium, and lead ions, Ag$^+$ is among the most studied monovalent ions with PVC-based ISEs for ultratrace analysis. Therefore, a solid comparison base is available for conventional membrane matrixes, while at the same time, silver ionophores have never been tested in SR matrixes. Apparently, the best selectivities for most of the tested ions were obtained with o-xylylenebis(N,N-diisobutyl dithiocarbamate); ionophore[42] originally introduced as a copper(II) ionophore.[43] In contrast to the ETH 1001-based SR membranes, the dissolution of the silver ionophore in the ISM was facilitated by adding 5−15 wt % DOS.

Previous studies reported monovalent ion-selectivities approaching 10^{-12} for Na$^+$ (Table 2; values in parentheses for the AgSCISEs), but in general, the selectivities exceeded 10^{-8} for most of the studied interfering cations. Even so, the SR-based AgCWEs and AgSCISEs showed significantly better selectivities than reported either for PVC[42] or methyl methacrylate−decyl methacrylate[44]-based membranes. Interestingly, the AgCWEs had somewhat better selectivities than PANI-based AgSCISEs. This suggests that the PANI nanoparticles present in the SR membrane, as a result of the slight intermixing of the PANI and the SR membrane upon drop casting of the membrane, affect the silver selectivities.[45] This assumption was proved by determining the selectivity of AgISMs prepared by premixing the SR-based cocktail with PANI nanodispersion using the same amounts as for the AgSCISEs, but deposited as a single composite layer (Table 2). Though the selectivity coefficients worsened by ca. 3 orders of magnitude for all tested interferents, they remained in all cases better than −8.5 logarithmic units, which is still outstanding. While the slight intermixing of PANI and the outer SR membrane cannot be avoided (although it was minimized by reducing the excess of THF in the ion-selective cocktail), further mixing of the two layers after curing is very unlikely, as it has been proven earlier that nanoparticles are immobile even in highly plasticized linear PVC chain-based membranes.[46]

Figure 3 shows the changes in the calibration curve of initially unconditioned AgSCISEs (previously not exposed to Ag$^+$) upon repeated calibrations from low to high concentrations. As in the case of the CaISEs, a pronounced supernernstian response is visible, but due to the plasticizer content (and extraordinary

(39) Gyurcsanyi, R. E.; Linder, E. Cytometry, Part A 2006, 69A, 792–804.
(40) Bereczki, R.; Gyurcsanyi, R. E.; Agai, B.; Toth, K. Analyst 2005, 130, 63–70.
(41) Oh, B. K.; Kim, C. Y.; Lee, H. J.; Rho, K. L.; Cha, G. S.; Nam, H. Anal. Chem. 1996, 68, 503–508.
(42) Szigeti, Z.; Malon, A.; Vigassy, T.; Csokai, V.; Grun, A.; Wygladacz, K.; Ye, N.; Xu, C.; Chebny, V. J.; Bitter, I.; Rathore, R.; Bakker, E.; Pretsch, E. Anal. Chim. Acta 2006, 572, 1–10.
(43) Kamata, S.; Murata, H.; Kubo, Y.; Bhale, A. Analyst 1989, 114, 1029–1031.
(44) Chumbimuni-Torres, K. Y.; Rubinova, N.; Radu, A.; Kubota, L. T.; Bakker, E. Anal. Chem. 2006, 78, 1318–1322.
(45) Bobacka, J.; Lindfors, T.; McCarrick, M.; Ivaska, A.; Lewenstam, A. Anal. Chem. 1995, 67, 3819–3823.
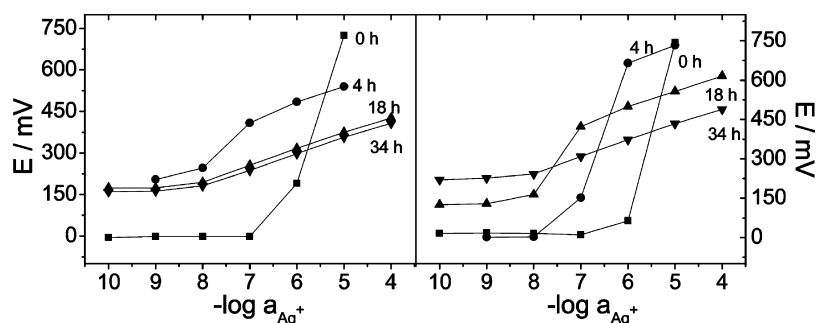(46) Jágerszki, G.; Grün, A.; Bitter, I.; Tóth, K.; Gyurcsányi, R. E. Chem. Commun. 2010, 46, 607–609.

Figure 3. Gradual disappearance of the supernernstian response of unconditioned Ag⁺-selective electrodes with (a) 5 μL and (b) 20 μL of membrane cocktail cast on the electrode surface. The membrane thicknesses were ~50 μm and ~200 μm, respectively. The time instances demark the start of the calibration curve from low to high concentrations.
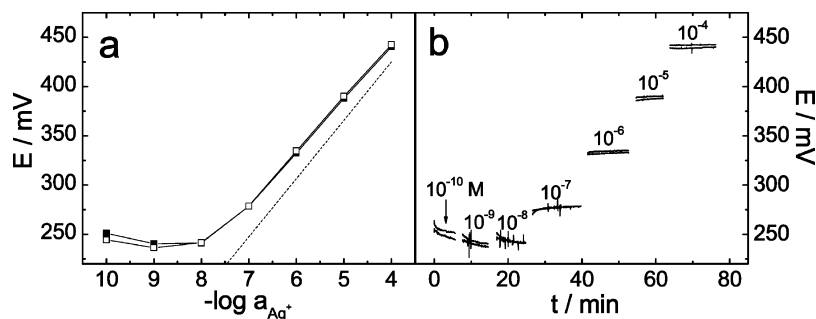

Figure 4. Calibration curves of two identically prepared AgSCISEs conditioned in 1 nM AgNO₃ (a) and their corresponding potential traces (b). The theoretical responses (25 °C) are denoted with the dashed lines.

Ag⁺-selectivities) this occurs at higher concentrations, i.e., as high as 10^{-5} M, suggesting that the ion mobility in these membranes is much higher than in those based on unplasticized SRs. This has been confirmed by using the recently introduced chronopotentiometric method[47,48] for the determination of ionophore diffusion coefficients in the membrane. As there is little difference among the diffusion coefficients of different ionophores in identical membrane compositions,[48] and due to the better solubility of the calcium ionophore ETH 1001 in the SR matrix, the ionophore diffusion coefficient was determined with this ionophore in 10 wt % DOS-containing and DOS-free SR membranes. The diffusion coefficient of ETH 1001 was found to be ca. 3 orders of magnitude smaller in the DOS-free membranes ($6 \times 10^{-12} \pm 5 \times 10^{-12}$ cm² s⁻¹) than in those containing 10 wt % DOS ($6.3 \times 10^{-9} \pm 5 \times 10^{-10}$ cm² s⁻¹). The results show unambiguously that while the diffusion coefficient of the free ionophore in the SR membranes containing DOS is similar to those found in conventional PVC membranes,[7,49] the diffusion coefficient in the pure SR matrixes approaches those reported for PA membranes.[18] Figure 3 shows the gradual disappearance of the supernernstian response upon repeated calibrations which is highly dependent on the membrane thickness, but for thicknesses of less than 250 μm, the Nernstian response established within 34 h. Subjecting the electrodes to the same conditioning procedure (10^{-9} M AgNO₃; see Experimental Section) as described for

the Ca²⁺-selective membranes, the detection limit was 2×10^{-8} M with excellent potential reproducibility between the different electrodes (Figure 4). The relatively high LOD is somewhat unsatisfactory when considering the extraordinary selectivities of the AgSCISEs. While certainly the higher diffusivity of the DOS-containing SR membranes adversely affects the LOD, the reason for such a high LOD is not fully clear when the predicted static LOD is around 1 fM. Interestingly, this is the case with most Ag⁺-selective electrodes based on the same ionophore but different membrane matrixes, i.e., their LODs are generally higher than 1 nM. This raises the question whether the strong silver complexation could cause partial decomposition of the active membrane components leading to the decrease of the Ag⁺-selectivity. Unfortunately, this assumption cannot be tested, as the unbiased selectivity coefficients cannot be remeasured once the AgISMs have been exposed to silver and the conventional selectivity coefficients are inherently inferior to the unbiased selectivity coefficients. It should be pointed out, however, that the SR-based AgCWEs and AgSCISEs were superior in every aspect to PVC formulated membranes (Table 1).

Potentiometric Aqueous Layer Test. While a good short-term stability and good potentiometric characteristics were obtained for the SR-based SCISEs, their long-term stability might be influenced by formation of an aqueous layer beneath the membrane. This possibility was investigated by using the so-called potentiometric aqueous layer test introduced by the Pretsch group.[24] The test is based on detecting potential drifts upon changing from a primary ion solution to a highly concentrated interfering ion solution and then back to the primary ion solution. If an aqueous layer is formed beneath the membrane, the ionic

(47) Zook, J. M.; Buck, R. P.; Gyurcsányi, R. E.; Lindner, E. *Electroanalysis* **2008**, *20*, 259–269.
(48) Bodor, S.; Zook, J. M.; Lindner, E.; Tóth, K.; Gyurcsányi, E. R. *J. Solid State Electrochem.* **2009**, *13*, 171–179.
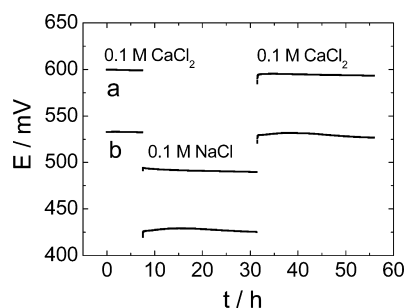(49) Pendley, B. D.; Gyurcsányi, R. E.; Buck, R. P.; Lindner, E. *Anal. Chem.* **2001**, *73*, 4599–4606.

Figure 5. Aqueous layer test for (a) a CaSCISE and (b) a CaCWE.

composition of the aqueous layer will also be changed by the transmembrane ion fluxes leading to characteristic potential drifts. The extraordinary silver selectivities of the AgSCISEs and AgCWEs make a significant reconditioning of the membranes with interfering ions practically impossible and thus prohibit the use of the aqueous layer test which was therefore performed only with Ca^{2+}-electrodes. The driftless potential responses shown in Figure 5 indicate the absence of aqueous layers for both CaSCISEs and CaCWEs. This is in good accordance with recently published results of the low water uptake of a 267 μm thick SR-based CaCWE measured by FTIR-ATR for the same membrane composition as in this study.[26] The diffusion coefficients of water in the SR-based CaCWE membrane ($D_1 = 2.2 \times 10^{-7}$ cm^2 s^{-1}; $D_2 = 1.3 \times 10^{-8}$ cm^2 s^{-1}) and the plasticized PVC membrane ($D_1 = 1.4 \times 10^{-7}$ cm^2 s^{-1}; $D_2 = 1.2 \times 10^{-8}$ cm^2 s^{-1}) were very similar but the total water uptake at equilibrium (at an infinite time) was ~3 times lower for the SR-based CaCWE in comparison to the PVC-based counterpart[4] (plasticized with DOS containing 0.8 wt % calcium ionophore IV (ETH 5234) and 0.45 wt % KTFPB). The D_1 was related to the diffusion process of monomeric and dimeric water, and D_2 to clustered and bulk water.[26]

Oxygen and Light Sensitivity. The influence of dissolved O_2 on the potentiometric responses of thinner spin-coated calcium CWEs and SCISEs (membrane thickness: ~60 μm) was tested by purging N_2 gas through a stirred 1 mM CaCl$_2$ solution for 30 min (data not shown). The potential of all electrodes, including the CWEs, were stable throughout the test which may indicate again the absence of a water layer beneath the SR membranes. As pointed out by Buck, the water permeating through the membrane is a major obstacle for the potential stabilizing processes at solid conductor/membrane interfaces.[50] No redox sensitivity of the CaSCISEs (<3.5 mV; data not shown) were observed in 1 mM CaCl$_2$ by varying the ratio of Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ at a total concentration of 2 mM whereas the potential of a Pt electrode changed 346 mV in the used concentration ratio interval. As uncoated PANI films showed also a large potential change of 99 mV,[37] the lack of redox sensitivity of the SCISE indicates that PANI does not form an interpenetrating network in the outer silicone rubber matrix, in contrast to the "single-piece electrode" concept.[45]

Importantly, no light sensitivity of the potentiometric response was observed for the CaSCISEs ($n = 3$) when exposed to intensive illumination by placing a 20 W halogen lamp at a distance of ca.
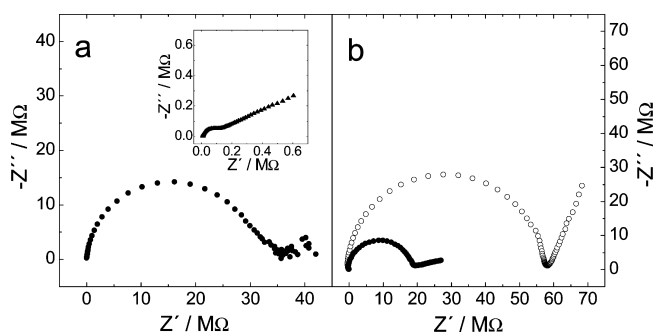

Figure 6. Impedance spectra measured in 1 mM CaCl$_2$: (a) CaSCISE (●) and PANI (D1003) (insert); (b) AgSCISE (●) and AgCWE (○). f = 100 kHz to 10 mHz; ΔE_{ac} = 100 mV [PANI (D1003): ΔE_{ac} = 10 mV].
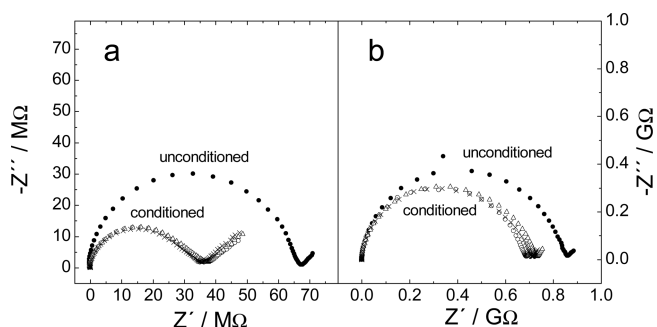

Figure 7. The impedance spectra measured over 4 days in 1 mM CaCl$_2$: (a) CaSCISE and (b) CaCWE. (●) Unconditioned membrane, (○) measured at day 2, (△) day 3, and (×) day 4; f = 100 kHz to 10 mHz; ΔE_{ac} = 100 mV.

5 cm for 10 min, which is in good accordance with the observed light insensitivity of PANI(D1003).[51] This is remarkable, as one of the major limitations of using CP as solid contacts is their marked sensitivity to light.

Impedance Measurements. The PANI solid-contact layer without the outer SR membrane had the lowest bulk resistance (R_b) (Figure 6a; insert), which increased to $R_b \cong 35$ MΩ for the CaSCISEs (Figure 6a). In comparison, the resistance of an unconditioned CaCWE is ~900 MΩ (Figure 7b), whereas it is ~65 MΩ for an unconditioned CaSCISE (Figure 7a). The resistance of both membranes stabilized within 1−2 days. After two days, the resistance of the CaSCISE was 1/20 (~35 MΩ) of that of the CaCWE (~700 MΩ). The reason for the lower resistance of CaSCISEs is that PANI dissolved slightly in the upper SR-based CaISM. Impedance measurements showed that the bulk resistance of an unconditioned SR membrane decreased by ca. 50% when 5 wt % of PANI was dispersed homogenously into the SR membrane (results not shown here). The mechanism by which PANI lowered the bulk resistance is unclear. However, it is possible that similar to the lipophilic additives in ISMs, the addition of positively charged PANI and its negatively charged counterions to the SR membrane may slightly increase the concentration of cationic and anionic sites in the CaISM, which increases its polarity (dielectric constant) and thus lowers the resistance of the membrane. It was previously reported that the addition of 1−10 wt % PANI to plasticized PVC membranes lowered the bulk

(50) Buck, R. P. *Anal. Chem.* **1978**, *50*, 17R–29R.

(51) Lindfors, T. *J. Solid State Electrochem.* **2009**, *13*, 77–89.
(52) Lindfors, T.; Bobacka, J.; Lewenstam, A.; Ivaska, A. *Analyst* **1996**, *121*, 1823–1827.

resistance of the membranes in comparison to a CWE.[45,52] However, this was not the same type of PANI that was used in this work. As was already pointed out, this is advantageous for obtaining electrodes with low noise levels and good mechanical strength of the PANI/SR interface. The resistance of the AgCWE ($R_b \cong 60$ MΩ) was ca. 1/12 of the resistance of the CaCWE (Figures 6b and 7b). The reason is that DOS added to the membrane (10 wt %) lowers the resistance of the AgCWE. As in case of the CaSCISEs, the SC layer lowered the resistance of the AgSCISEs ($R_b \cong 20$ MΩ) for similar reasons. However, due to the inherently much lower membrane resistance of the DOS-containing membranes, the effect is less significant than for the Ca^{2+}-selective electrodes.

CONCLUSIONS

This study shows that CaSCISEs and AgSCISEs with detection limits of 2×10^{-9} M and 2×10^{-8} M, respectively, can be prepared with SR as the outer ISM and PANI (D1003) as the SC layer. Both types of electrodes had good potential reproducibility and selectivity, which in case of the Ag$^+$-selective membranes exceeds any selectivities reported for monovalent interferents.

Impedance measurements reveal that PANI lowered the resistance of the CaSCISEs ($R_b \cong 35$ MΩ) and AgSCISEs ($R_b \cong 20$ MΩ) compared to the CaCWEs ($R_b \cong 700$ MΩ) and AgCWEs ($R_b \cong 60$ MΩ), which was shown to be beneficial for preparing SCISEs with low noise levels. The reason for the decreased resistance is the slight dissolution of PANI in the SR membrane. Other major benefits of the SCISEs based on PANI and SR are their good E^0 reproducibility, light insensitivity of their potential response, and the absence of an aqueous layer beneath the SR membranes.