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# Determination of Water Uptake of Polymeric Ion-Selective Membranes with the Coulometric Karl Fischer and FT-IR-Attenuated Total Reflection Techniques

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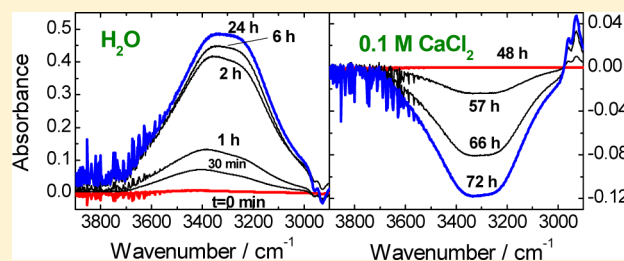
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## Supporting Information

**ABSTRACT:** The water uptake of plasticized poly(vinyl chloride) (PVC) and silicone rubber (SR) based calcium-selective membranes which are commonly used in solid-contact and coated-wire ion-selective electrodes (SC-ISEs and CWEs) was quantified with the oven based coulometric Karl Fischer (KF) technique. Two different membrane types were studied: (1) the plasticized PVC or SR (RTV 3140) membrane matrix without other added membrane components and (2) the full  $\text{Ca}^{2+}$ -selective membrane formulation consisting of the membrane matrixes, potassium tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate and calcium ionophore IV (ETH 5234) or calcium ionophore I (ETH 1001). The membranes were contacted for 24 h either asymmetrically from one side or symmetrically from both sides with deionized water (DIW) or 0.1 M solutions of  $\text{CaCl}_2$ ,  $\text{KCl}$ , or  $\text{NaCl}$ . It was found that the water uptake was higher for symmetrically contacted membranes. The highest water uptake (0.15–0.17 wt %) was obtained for the plasticized PVC based  $\text{Ca}^{2+}$ -selective membranes in DIW, whereas the water uptake was lower in 0.1 M electrolyte solutions. Symmetrically contacted  $\text{Ca}^{2+}$ -selective SR membranes had much lower water uptake in 0.1 M  $\text{CaCl}_2$  (0.03 wt %) than their plasticized PVC counterparts (0.1 wt %). However, the (noncontacted) SR membranes contained initially much more water (0.09–0.15 wt %) than the PVC membranes (0.04–0.07 wt %). Furthermore, in good accordance with the KF measurements, it was verified with FT-IR-attenuated total reflection (ATR) spectroscopy that the water content at the substrate/membrane interface and consequently in the whole membrane was influenced by the electrolyte solution.



Poly(vinyl chloride) (PVC) based ion-selective membranes (ISMs) are commonly used in potentiometric ion-selective electrodes (ISEs) and selective optodes.<sup>1–3</sup> Silicone rubber (SR) was introduced already in the 1970s as an ISM matrix for  $\text{K}^+$ -selective ISEs but has been studied much less than plasticized PVC based ISMs.<sup>4</sup> Some drawbacks of PVC based ISMs are leaching of the plasticizer,<sup>5,6</sup> ionophore,<sup>7</sup> and other additives from the ISM to the solution phase<sup>8,9</sup> influencing the response stability of ISEs. Also due to the water uptake of the ISMs, thin aqueous layers or pools of water can be formed at the electrode interfaces in potentiometric solid-contact ion-selective electrodes (SC-ISEs) and coated-wire electrodes (CWEs) resulting in transmembrane ion fluxes<sup>10,11</sup> and potential instability.<sup>12</sup> The aqueous layer or pools of water behave as electrolyte reservoirs resulting in a re-equilibration of ions between these reservoirs and the outer sample solution.<sup>10</sup> Hence, this will affect the long-term stability, the detection limits, and the selectivity of the SC-ISEs and CWEs.<sup>6</sup> It is therefore crucial to be able to quantify the water uptake and use

ISMs with low water uptake to obtain electrodes with more stable response characteristics.

The water flux (diffusion) in polymers is mainly driven by the hydrostatic pressure, electric field,<sup>13</sup> polarity of the polymer chains,<sup>14</sup> and the osmotic pressure (concentration gradient) for the particular polymer–electrolyte system.<sup>13</sup> The osmotic pressure driven water and ion fluxes result finally in equilibrium between the polymer and the electrolyte solution described by the isotonic state in which the chemical potentials of the membrane and solution phases are equal. The water uptake of polymers is also expected to be influenced by the polarity of the plasticizer. ISMs prepared with a polar plasticizer should facilitate the water uptake due to the polar nature of water. In polymeric ISMs, the ion–ionophore complexation takes place at the very interface of the ISM/solution and the ions will consequently leave their hydration shell before entering the

Received: September 25, 2012

Accepted: December 18, 2012

Published: December 18, 2012



ISM phase.<sup>15</sup> A theoretical study of the calcium ion transfer across a water/nitrobenzene (NB) interface showed that the first hydration shell of  $\text{Ca}^{2+}$  remains intact but the second shell suffers a severe water loss when  $\text{Ca}^{2+}$  is transferred from the aqueous to the NB phase.<sup>16</sup> The second hydration shell of the  $\text{Ca}^{2+}$  ions was gradually replaced with NB as a function of a distance from the interface. Similarly, in nonselective polymeric membranes without ionophores, the loss of the hydration shell of ions is associated with the ability of water to be replaced with molecules or ions which are present in the membrane phase, for example, the plasticizer molecules. This will most likely facilitate the uptake of ions and thus increase the water content of the polymeric matrix.

The water uptake of plasticized PVC based ISMs has been previously studied by Harrison et al. in the 1990s.<sup>17,18</sup> They concluded from NMR studies that at least two types of water were present in the ISM: “freezable” (droplets and clusters) and “nonfreezable” (dissolved and matrix bound) water. In poly(*n*-butylacrylate) based ISMs, the water transport has been studied with a holographic method.<sup>19</sup> More recently, it was shown with FT-IR-attenuated total reflection (ATR) spectroscopy that monomeric, dimeric, clustered, and bulk water were present in the plasticized PVC and SR based ISMs.<sup>3,20</sup> In these studies, it was found that the water uptake of SR membranes was lower than for the plasticized PVC membranes. The aqueous layer formation in SC-ISEs was also very recently studied by different techniques, e.g., neutron reflectometry, electrochemical impedance spectroscopy (EIS), and secondary-ion mass spectrometry.<sup>6,21–23</sup> The aqueous layer formation could be prevented using a combination of poly(3-octylthiophene) (POT) as the ion-to-electron transducing solid-contact (SC) layer and outer ISMs consisting of a copolymer of poly(methyl methacrylate)–poly(decyl methacrylate) (PMMA-PDMA). It was also shown in a separate study with FT-IR-ATR spectroscopy that POT lowered the water uptake of PMMA-PDMA.<sup>24</sup> When POT was replaced with a SC layer consisting of poly(3,4-ethylenedioxythiophene) having poly(styrene sulfonate) as counteranion, water was accumulated in the SC layer making the SC-ISE resemble a hydrogel or liquid contact ISE in its analytical performance.<sup>21</sup> In addition to the more sophisticated techniques listed above, gravimetric methods have been widely used to study the water uptake of polymeric materials.<sup>25</sup>

A hyphenated technique based on EIS and FT-IR-ATR spectroscopy was recently applied to study the influence of the water uptake of ISMs on the potential stability of SC-ISEs.<sup>11,12</sup> It was found that SC-ISEs having POT as SC and an outer ISM consisting of SR had superior potential stability. The SR membranes consisted of 98.1 wt % SR (RTV 3140), 1.0 wt % calcium ionophore I (ETH 1001), and 0.9 wt % potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTFPB).<sup>12</sup> FT-IR-ATR measurements showed that the POT layer in combination with the hydrophobic SR-ISM functioned as an effective water barrier preventing water from reaching the substrate/SC interface. Mathematical modeling showed that the water diffusion coefficients in the outer SR membrane were ca.  $5 \times 10^{-8}$ – $5 \times 10^{-10}$   $\text{cm}^2\text{s}^{-1}$  but ca. 2 orders of magnitude lower in the SC layer of POT.<sup>12</sup> The POT-SR based SCISEs had practically driftless and very stable potentials during the test period of 24 h in contact with 0.1 M  $\text{CaCl}_2$  indicating that they can be used directly without preconditioning in contrary to plasticized PVC based ISMs that normally require an overnight conditioning prior to use.<sup>12</sup> SR and poly(aniline) based SC-

ISEs having low water uptake have previously shown to be beneficial in achieving a low detection limit of  $10^{-9}$  M  $\text{Ca}^{2+}$ .<sup>26</sup>

In this study, the water uptake was studied with the oven based coulometric Karl Fischer (KF) technique for the plasticized PVC or SR (RTV 3140) matrixes and for the full  $\text{Ca}^{2+}$ -selective membrane formulation consisting of the membrane matrix, KTFPB and either calcium ionophore IV (ETH 5234) or calcium ionophore I. For accurate assessment of trace levels of water (ppm), the coulometric KF method is the most frequently used method.<sup>27</sup> The membranes were contacted for 24 h either asymmetrically from one side or symmetrically from both sides with deionized water (DIW) or 0.1 M solutions of  $\text{CaCl}_2$ , KCl, or NaCl. The results obtained with the KF titrations of the different membrane types have been compared qualitatively with the water uptake measured with the FT-IR-ATR technique. Both positive and negative water absorption bands were observed in the FT-IR spectra when the membranes were contacted with different electrolyte solutions. To the best of our knowledge, this has not been previously reported for ISMs. This indicates that the electrolyte solution affects the water uptake of the membranes.

## ■ EXPERIMENTAL SECTION

**Chemicals.** High molecular weight PVC, bis(2-ethylhexyl) sebacate (DOS), KTFPB, ETH 5234, ETH 1001, and tetrahydrofuran (THF), all of Selectophore grade, were received from Fluka, as well as the Hydranal-Coulomat AG Oven KF reagent. Room temperature vulcanizing silicone rubber (RTV 3140) was obtained from Dow Corning.

**Membrane Preparation.** Five different membrane types were studied with the following compositions: (Type 1) PVC matrix: 33.3 wt % PVC and 66.7 wt % DOS, (PVC/DOS, 1:2); (Types 2 and 3) PVC based  $\text{Ca}^{2+}$ -selective membranes containing 98.75 wt % PVC/DOS (1:2), 0.45 wt % KTFPB, and 0.8 wt % calcium ionophore IV (CaISM(PVC-IV)) or calcium ionophore I (CaISM(PVC-I)); (Type 4) SR matrix: 100 wt % RTV 3140; (Type 5) SR based  $\text{Ca}^{2+}$ -selective membranes containing 98.1 wt % RTV 3140, 0.9 wt % KTFPB, and 1.0 wt % calcium ionophore I (CaISM(SR-I)). The components were dissolved in THF solutions with a dry weight of 20 wt %.

In the KF measurements, the thicknesses of the circular PVC and SR based membranes ( $d = 15$  mm) measured with a micrometer (precision: 1  $\mu\text{m}$ ) were 280–320 and 260–300  $\mu\text{m}$ , respectively, whereas the membrane thicknesses in the FT-IR-ATR measurements were either ca. 100 or 300  $\mu\text{m}$  for both membrane types (see Supporting Information). Before starting the KF and FT-IR-ATR measurements, the THF in the PVC membranes were allowed to evaporate overnight and the SR membranes were (moisture) cured in contact with air for 3 days.

### Oven Based Coulometric Karl Fischer Titrations.

Before the KF measurements were conducted, the membranes were contacted for 24 h either asymmetrically (from one side) or symmetrically (from both sides) with DIW or 0.1 M solutions of  $\text{CaCl}_2$ , KCl, or NaCl and thereafter carefully dried on both sides with dust free paper for ca. 30 s to remove water droplets from the membrane surfaces. The membranes were then sealed in glass bottles which were placed in the sample holder of the KF oven compartment. Due to the relatively low water content of the studied membranes, three membranes with a total mass of ca. 0.15 g were always measured together in one measurement to increase the sample mass and con-

**Table 1.** Water Uptake of PVC and SR Membranes Symmetrically Contacted for 24 h with DIW and 0.1 M Solutions of  $\text{CaCl}_2$ , NaCl, and KCl ( $n = 3$ )

membrane type	DIW (ppm)	RSD (%)	0.1 M $\text{CaCl}_2$ (ppm)	RSD (%)	0.1 M NaCl (ppm)	RSD (%)	0.1 M KCl (ppm)	RSD (%)
PVC matrix	700 $\pm$ 230	33	470 $\pm$ 220	47	480 $\pm$ 230	48	460 $\pm$ 230	50
CaISM(PVC-IV)	1470 $\pm$ 710	48	970 $\pm$ 450	46	930 $\pm$ 150	16	830 $\pm$ 460	55
CaISM(PVC-I)	1660 $\pm$ 370	22	850 $\pm$ 410	48	not measured		not measured	
SR matrix	190 $\pm$ 80	42	290 $\pm$ 50	17	220 $\pm$ 100	45	220 $\pm$ 50	23
CaISM(SR-I)	310 $\pm$ 500	161	350 $\pm$ 380	109	210 $\pm$ 540	257	not measured	

sequently the accuracy and reliability of the measurements. Three parallel measurements were always carried out to obtain the relative standard deviation. The water release of the PVC and SR membranes were measured at 110 and 250 °C, respectively (see Supporting Information), and the water uptake was calculated as the difference in the water content of membranes contacted with the aqueous solutions and the noncontacted as prepared membranes.

**FT-IR-ATR Measurements.** In the FT-IR-ATR setup, the membranes were in contact with the electrolyte solution only from one side thus mimicking the asymmetrical KF measurements. The details of the FT-IR-ATR measurements have been described elsewhere<sup>20</sup> and in the Supporting Information. The strong OH stretching bands of water at ca. 2950–3750  $\text{cm}^{-1}$  were used to monitor the water uptake. To monitor the influence of electrolyte solutions on the water content at the ZnSe/membrane interface of membranes which were fully conditioned in DIW, the FT-IR-ATR measurements were usually carried out continuously for 96 h in the following measuring sequence: (1) DIW (48 h), (2) 0.1 M electrolyte solution (24 h), and (3) DIW (24 h). In some cases, the measurements were also carried out with the modified sequence: (1) 0.1 M  $\text{CaCl}_2$  (48 h), (2) 0.1 M NaCl (24 h), and (3) 0.1 M  $\text{CaCl}_2$  (24 h). A new background was recorded each time before changing the solution.

## ■ RESULTS AND DISCUSSION

**Oven Based Coulometric Karl Fischer Measurements.** *Plasticized PVC Based ISMs.* Water in the chemicals used for the membrane preparation was determined at 110 °C to evaluate their influence on the water content of the PVC membranes. It was found that the water content of the PVC powder, the plasticizer (DOS), and THF was 220  $\pm$  10, 540  $\pm$  50, and 1490  $\pm$  75 ppm ( $n = 3$ ), respectively. Calculated from these mean values and the membrane preparation parameters given in the Supporting Information, the water content in the as prepared PVC matrix (only PVC/DOS = 1:2; not contacted with aqueous solutions) was expected to be 6390 ppm assuming that all water from the chemicals used for the membrane preparation stay within the formed PVC matrix. However, the oven based coulometric Karl Fischer measurements showed that the water content was only 610  $\pm$  20 ppm for the as prepared PVC matrix (see Supporting Information). It indicates that most of the water in the PVC membranes originating from residual water in the components used for the membrane preparation evaporates together with THF during the overnight drying of the membranes.

As the membranes were in contact with atmospheric air during the overnight drying process, the humidity in air may influence the water content of the membranes. The PVC matrixes were therefore left in contact with air for 48 h. It was found that humidity had negligible influence on the water content of the membranes during this contacting time.

However, if the chemicals used for the membrane preparation are not stored under nitrogen atmosphere, their water content will slowly increase due to exposure to humidity, thus increasing the initial water content of the noncontacted plasticized PVC membranes.

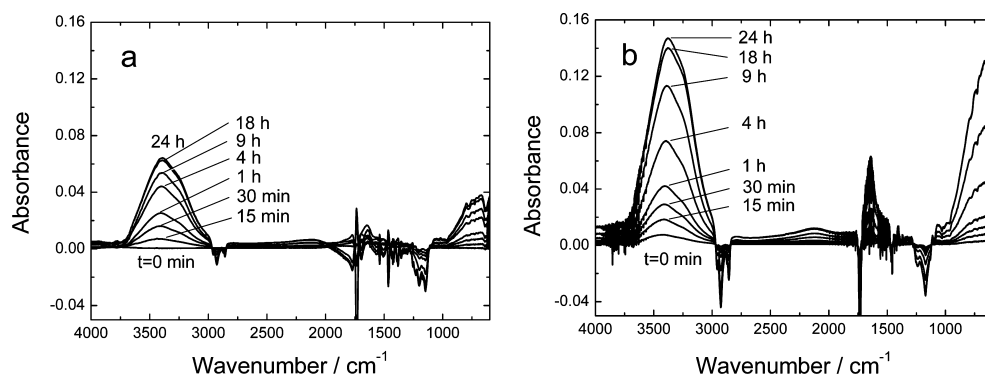
The water uptake of the PVC matrixes, which were *symmetrically* contacted for 12, 24, and 48 h with DIW and 0.1 M  $\text{CaCl}_2$ , was compared to find the optimum contacting time. The steady-state was reached within 24 h and was therefore chosen as the contact time for all other measurements. The water uptake of the symmetrically contacted PVC matrix, CaISM(PVC-IV) and CaISM(PVC-I) in DIW, and 0.1 M solutions of  $\text{CaCl}_2$ , NaCl, and KCl is shown in Table 1. Since the CaIV ionophore is more lipophilic than CaI, it was included in this study to evaluate the influence of the ionophore on the water uptake. For the CaISM(PVC-I) membranes, the water uptake was measured only in DIW and 0.1 M  $\text{CaCl}_2$ . The relative standard deviation (RSD;  $n = 3$ ) for each individual KF measurement was for the PVC membranes between 4 and 36% (symmetrically contacted) and 2–21% (asymmetrically contacted) (see Supporting Information). For the SR membranes, the RSDs were between 4 and 41% (symmetrical) and 2–9% (asymmetrical). These RSD values are fairly reasonable considering the low sample mass of ca. 0.15 g. However, due to the low water uptake of the membrane formulations used in this work, the propagation of the errors results in relatively high RSDs when the water uptake for a specific membrane type was calculated as the difference in the water content of the membranes contacted with the aqueous solutions and the noncontacted as prepared membranes. This was especially pronounced for the asymmetrically contacted membranes having a very low water uptake.

As shown in Table 1, the water uptake of the symmetrically contacted PVC matrix was 700  $\pm$  230 ppm in DIW but 220–240 ppm lower in 0.1 M solutions of  $\text{CaCl}_2$ , NaCl, and KCl. Most likely, the lower osmotic pressure in 0.1 M electrolyte solutions results in lower water uptake of the PVC matrix in these solutions. Although the 0.1 M  $\text{CaCl}_2$  solution has higher osmolality (0.3 M) than the 0.1 M NaCl and 0.1 M KCl (0.2 M) solutions, it seems that it is not influencing the water uptake of the PVC membranes. In comparison to the PVC matrix consisting of only PVC and DOS, the water uptake of both CaISM(PVC-IV) and CaISM(PVC-I) was approximately two times higher (1470  $\pm$  710 and 1660  $\pm$  370 ppm) in deionized water, respectively (Table 1). In accordance with the PVC matrix, the water content of the CaISM(PVC-IV) and CaISM(PVC-I) was lower in the 0.1 M electrolyte solutions compared to DIW. For the CaISM(PVC-I), the water uptake in DIW was slightly higher than for the CaISM(PVC-IV), which can be explained by the lower lipophilicity of calcium ionophore I (ETH 1001) compared to calcium ionophore IV (ETH 5234). For both CaISM(PVC-IV) and CaISM(PVC-I), the incorporation of ionic and polar groups in the ISMs



Table 2. Water Uptake of PVC and SR Membranes Asymmetrically Contacted for 24 h with DIW and 0.1 M  $\text{CaCl}_2$  ( $n = 3$ )

membrane type	DIW (ppm)	RSD (%)	0.1 M $\text{CaCl}_2$ (ppm)	RSD (%)
PVC matrix	$220 \pm 300$	136	$80 \pm 90$	112
CaISM(PVC-IV)	$240 \pm 210$	88	$30 \pm 60$	200
SR matrix	$90 \pm 70$	78	$150 \pm 70$	47
CaISM(SR-I)	$180 \pm 170$	94	$200 \pm 170$	85

Figure 1. FT-IR-ATR spectra of (a) the PVC matrix (thickness:  $304 \mu\text{m}$ ) and (b) the CaISM(PVC-IV) membrane ( $288 \mu\text{m}$ ) asymmetrically contacted with DIW for 24 h.

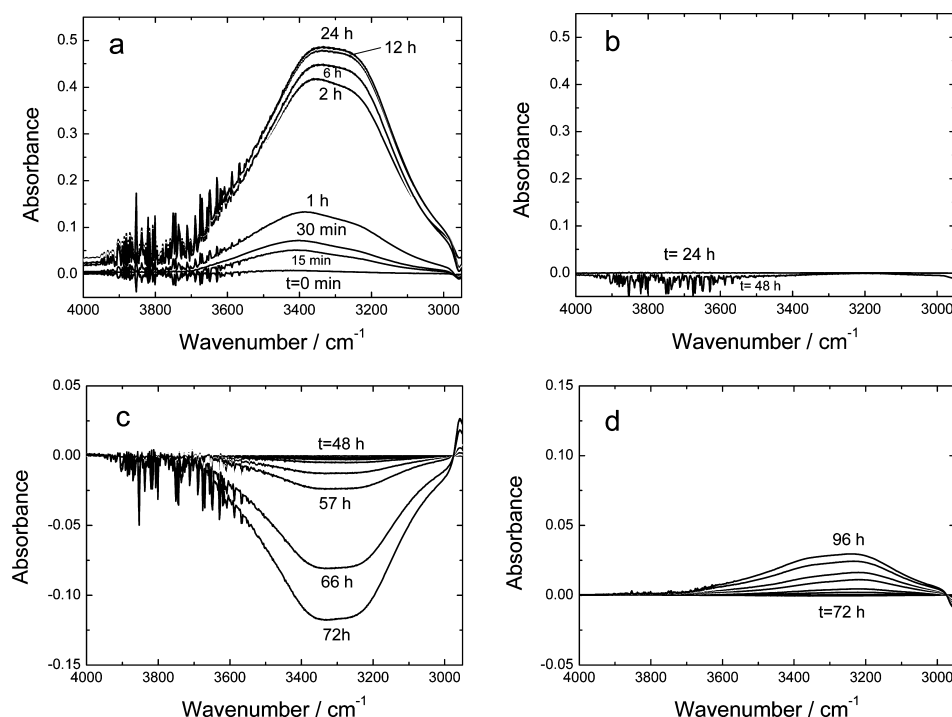
(KTFPB, ETH 5234, and ETH 1001) increased the hydrophilicity and polarity of the ISMs and thus increased the water uptake compared to the PVC matrix containing only PVC and DOS.

The water content of the PVC matrix and CaISM(PVC-IV) which were *asymmetrically* contacted in DIW and 0.1 M  $\text{CaCl}_2$  is shown in Table 2. The water uptake of the asymmetrically contacted membranes mimic the water uptake process taking place in the FT-IR-ATR measurements in which the membranes were asymmetrically contacted only from one side with the electrolyte solutions. Although the water uptake of the asymmetrically contacted membranes was very low and the RSDs are very high, the same trend as for the symmetrically contacted membranes can be distinguished with higher water uptake in DIW compared to 0.1 M  $\text{CaCl}_2$ . The water uptake in other electrolyte solutions than  $\text{CaCl}_2$  was not determined due to the similar water uptake of symmetrically contacted membranes in 0.1 M solutions of  $\text{CaCl}_2$ ,  $\text{NaCl}$ , and  $\text{KCl}$  (Table 1). The very low water uptake of the PVC matrix and CaISM(PVC-IV) in 0.1 M  $\text{CaCl}_2$  indicates that both membrane types were rather hydrophobic (Table 2). In contrast to the symmetrically contacted membranes (Table 1), there were no clear differences in the water uptake of the PVC matrix and CaISM(PVC-IV). This is probably due to the very low water uptake of both membranes. It was previously shown that very low water content at the electrode substrate/SC interface in SC-ISEs had significant impact on obtaining superior potentiometric response stability.<sup>12</sup> The low water uptake of the asymmetrically contacted membranes is therefore beneficial for SC-ISEs.

**Silicone Rubber Based ISMs.** The water content of the *symmetrically* contacted SR matrix and CaISM(SR-I) is shown in Table 1. Although the CaISM(SR-I) has a very high RSD, the SR membranes have in general much lower water uptake than their PVC counterparts, which is in good accordance with previously published results obtained with the FT-IR-ATR technique.<sup>3</sup> In the present work, a clear trend cannot be distinguished in the water uptake between the SR matrix and CaISM(SR-I). It seems that the water uptake of both

membrane types is independent of the contacting solution. Interestingly, it was found that the as-prepared SR membranes (not contacted with aqueous solutions) contained initially more water than the as prepared PVC membranes probably due to the moisture cured RTV 3140 formulation that was used for the SR membrane preparation. The water content of the noncontacted SR matrix and CaISM(SR-I) was 870–1030 ppm and 940–1500 ppm, respectively, whereas the noncontacted PVC matrix, CaISM(PVC-IV), and CaISM(PVC-I) had a water content of 370–670 ppm (see Supporting Information). Hence, the total water content of the SR membranes was in most cases even slightly higher than for the PVC membranes after contacting the membranes with the aqueous solutions. For example, the total water content of PVC and SR matrix membranes symmetrically contacted with DIW was  $1310 \pm 220$  and  $1220 \pm 60$  ppm, respectively (see Supporting Information). The corresponding values were  $1080 \pm 240$  and  $1320 \pm 30$  ppm in 0.1 M  $\text{CaCl}_2$ . Consequently, the higher initial water content of noncontacted SR membranes results in lower water uptake probably due to the lower osmotic pressure in comparison to the noncontacted PVC based membranes which contain less water. It is assumed that the uncured SR resin (RTV 3140) contained initially only negligible traces of water. Its water content could not be determined with the oven based coulometric KF technique because the SR resin started to cure immediately in the oven compartment during the measurement, thus consuming the trapped air in the measuring vessel resulting in negative water uptake compared to the background measurement.

The difference in the total water content for *asymmetrically* contacted membranes was even more pronounced between PVC and SR membranes. The SR matrix contacted with 0.1 M  $\text{CaCl}_2$  had approximately two times higher total water content ( $1020 \pm 20$  ppm) than the PVC membranes ( $490 \pm 50$  ppm) (see Supporting Information). For the asymmetrically contacted SR membranes in general, the water uptake is very low and almost in the same concentration range as for the PVC membranes in DIW (Table 2). The data in Table 2 indicate that the water uptake of the symmetrically contacted SR



**Figure 2.** FT-IR-ATR spectra of the CaISM(PVC-IV) membrane (thickness: 95  $\mu\text{m}$ ) continuously contacted for 96 h in the following sequence: (a, b) DIW (0–48 h), (c) 0.1 M  $\text{CaCl}_2$  (48–72 h), and (d) DIW (72–96 h).

membranes is independent of the contacting solutions. However, no definite conclusions can be made due to the high RSDs associated with all membrane types in Table 2.

**FT-IR-ATR Measurements. Plasticized PVC Based ISMs.** The FT-IR-ATR spectra shown in Figure 1 of the PVC matrix (thickness: 304  $\mu\text{m}$ ) and CaISM(PVC-IV) (288  $\mu\text{m}$ ) were measured in DIW for 24 h. The strong OH stretching band in the wavenumber region of 2950–3750  $\text{cm}^{-1}$  was used to monitor the water uptake. Additional water bands can be distinguished in the spectra at <1000  $\text{cm}^{-1}$ , 1640–1645  $\text{cm}^{-1}$  (OH bending vibrations),<sup>28</sup> and  $\sim 2125$   $\text{cm}^{-1}$  (broad peak). The spectra in Figure 1, which are in good accordance with the results of the coulometric KF measurements, show that the CaISM(PVC-IV) had higher water uptake compared to the PVC matrix. The downward pointing negative bands in the FT-IR spectra are related to the PVC/DOS membrane matrix which slightly swells during the water uptake, resulting in a decrease of the molar fraction of PVC/DOS.<sup>20</sup>

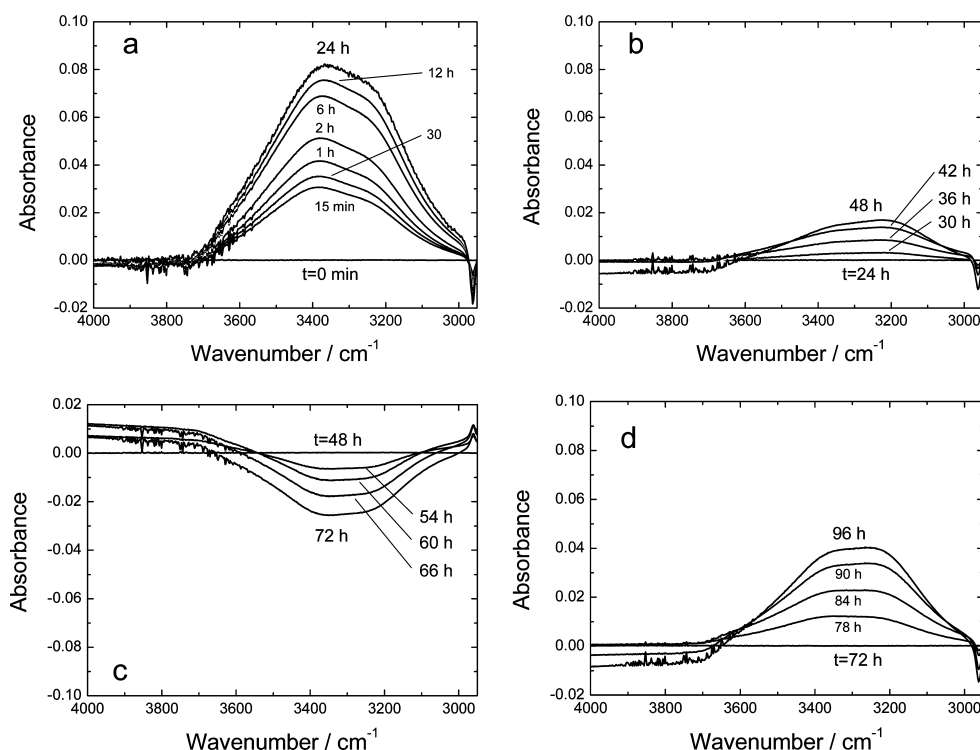
The water uptake of a 95  $\mu\text{m}$  thick CaISM(PVC-IV) membrane contacted with DIW and 0.1 M  $\text{CaCl}_2$  was studied continuously for 96 h. A thinner membrane than in Figure 1 (304  $\mu\text{m}$ ) was chosen for this study to increase the signal intensity (absorbance) due to the shorter diffusion time of water to the substrate/membrane interface. The CaISM(PVC-IV) was first contacted with DIW for 48 h to fully equilibrate and hydrate the membrane (Figure 2a,b). The FT-IR cell was then filled with 0.1 M  $\text{CaCl}_2$  for 24 h (Figure 2c; 48–72 h), and finally, the CaISM(PVC-IV) was contacted again with DIW for 24 h (Figure 2d; 72–96 h). As shown in Figure 2a, the water uptake is very quick in DIW and the membrane has almost reached the equilibrium already after 2 h. Only a minor increase in the absorbance was observed during the rest of the contacting time of the first 24 h. A new background was measured after 24 h, and practically, no water uptake was

observed during the following 24 h (24–48 h) showing that the membrane was fully equilibrated (Figure 2b).

When DIW in the measuring cell was replaced with 0.1 M  $\text{CaCl}_2$  (48–72 h), the intensity of the OH stretching bands at 2950–3750  $\text{cm}^{-1}$  decreased (negative bands) implying transmembrane flux of water from the membrane to the solution phase due to the lower osmotic pressure in 0.1 M  $\text{CaCl}_2$  (Figure 2c). This is in good accordance with the results of the KF measurements which showed that the water uptake was lower in 0.1 M  $\text{CaCl}_2$  than in DIW (Tables 1 and 2). The FT-IR spectra shown in Figure 2c indicate that the CaISM(PVC-IV) responds very slowly (within several hours) to the change in osmotic pressure and can therefore influence the long-term potential stability of CWE and SC-ISEs.

In the last measuring sequence of the FT-IR-ATR measurements (72–96 h), the CaISM(PVC-IV) is contacted again with DIW and the opposite phenomenon was observed with increasing water bands. Similarly to the 0.1 M  $\text{CaCl}_2$  solution, the CaISM(PVC-IV) responds very slowly to the change in the osmotic pressure with a slow transmembrane flux of water into the membranes. The maximum absorbance in Figure 2d (ca. 0.03 A.U.) indicates that the water content of the CaISM(PVC-IV) could not be fully recovered in DIW after keeping the membrane in 0.1 M  $\text{CaCl}_2$ . The reason for this is currently not understood. However, the results presented in Figure 2 clearly show that the water uptake of CaISM(PVC-IV) was influenced by the electrolyte solution. With the FT-IR-ATR technique, the presence of water in the ISM is detected only at the substrate/ISM interface. However, due to the good correlation between the coulometric KF and FT-IR-ATR measurements, it is expected that the results obtained with the FT-IR-ATR technique reflect the water content in the entire membrane phase.

To study the difference in the water uptake of a PVC matrix (thickness: 328  $\mu\text{m}$ ) in 0.1 M  $\text{CaCl}_2$  and 0.1 M  $\text{NaCl}$ , the



**Figure 3.** FT-IR-ATR spectra of the CaISM(SR-I) (thickness: 118  $\mu\text{m}$ ) continuously contacted for 96 h in the following sequence: (a, b) DIW (0–48 h), (c) 0.1 M  $\text{CaCl}_2$  (48–72 h), and (d) DIW (72–96 h).

membrane was first contacted with 0.1 M  $\text{CaCl}_2$  for 48 h, followed by 0.1 M  $\text{NaCl}$  (48–72 h) and 0.1  $\text{CaCl}_2$  (72–96 h). It was found that the membrane reached a steady-state during the first 24 h, and the water uptake within the next 24 h (24–48 h) was negligible. Only very minor increase of the absorbance (0.007 A.U.) was detected in 0.1 M  $\text{NaCl}$  (48–72 h), and a corresponding decrease was detected when the PVC matrix was contacted with 0.1  $\text{CaCl}_2$  (72–96 h). It shows that the water uptake is practically the same in both 0.1 M  $\text{CaCl}_2$  and 0.1 M  $\text{NaCl}$  which is in accordance with the KF measurements (Table 1).

The water uptake of a 61  $\mu\text{m}$  thick CaISM(PVC-IV) membrane was also determined in a sequence consisting of 0.1 M  $\text{CaCl}_2$  (48 h), 0.1 M tetraethylammonium chloride ( $\text{Et}_4\text{NCl}$ ) (48–72 h), and 0.1 M  $\text{CaCl}_2$  (72–96 h). The FT-IR spectra in Figure S-1 (see Supporting Information) showed that the water uptake was slightly higher in  $\text{Et}_4\text{NCl}$  compared to  $\text{CaCl}_2$  demonstrating the general applicability of the FT-IR-ATR spectroscopy for measuring the water uptake of ISMs also in other electrolyte systems than DIW- $\text{CaCl}_2$  and  $\text{CaCl}_2$ - $\text{NaCl}$ .

**Silicone Rubber Based ISMs.** As shown in Figure 3, the CaISM(SR-I) (thickness: 118  $\mu\text{m}$ ) was exposed to the same measuring sequence as shown in Figure 2. In accordance with the asymmetric KF measurements and previous studies,<sup>3</sup> the FT-IR spectrum in Figure 3a shows that the water uptake of CaISM(SR-I) after 24 h in DIW is lower than for CaISM(PVC-IV) (Figure 2a). The water uptake increased to a minor extent during the next 24 h (24–48 h; Figure 3b), indicating that the water uptake is slower in SR than in plasticized PVC. Negative and positive water bands were observed in the FT-IR spectra when the CaISM(SR-I) were exposed to 0.1 M  $\text{CaCl}_2$  (48–72 h; Figure 3c) and DIW (72–96 h; Figure 3d), respectively. Hence, in contrast to the asymmetric KF measurements, the FT-IR measurements confirm that the water content at the

ZnSe/membrane interface and most likely also in the bulk of the membrane is affected by the electrolyte solution. The uncertainty is high for the KF data in Table 2 due to the low water uptake and sample mass. It is therefore expected that the water uptake measured with the FT-IR-ATR technique is more reliable because of its higher sensitivity compared to the oven based coulometric KF technique. Although the water uptake cannot be quantified with the FT-IR-ATR technique, it is shown in this paper that it is a powerful tool for studying the water uptake of ISMs in different types of electrolyte solutions.

## CONCLUSIONS

The water uptake of plasticized PVC and SR based ISMs was quantified with the oven based coulometric Karl Fischer technique. Depending on the membrane type, the water content in noncontacted SR membranes was initially nearly 2–4 times higher than in PVC membranes. Hence, due to lower osmotic pressure, the water uptake of the SR membranes was in general lower than for the PVC membranes. For the PVC based membranes, the highest water uptake was observed in DIW for the symmetrically contacted CaISM(PVC-IV) and CaISM-(PVC-I) membranes containing both an ionic additive and a calcium ionophore. It was found that the water uptake was lower in 0.1 M solutions of  $\text{CaCl}_2$ ,  $\text{NaCl}$ , and  $\text{KCl}$  compared to DIW probably due to the lower osmotic pressure in the 0.1 M electrolyte solutions.

The FT-IR-ATR measurements confirmed both for the PVC and SR membranes that the water content at the ZnSe substrate/membrane interface was influenced by the electrolyte solution which was reflected in either negative (decreasing) or positive (increasing) OH stretching bands at ca. 3750–2975  $\text{cm}^{-1}$ . To the best of our knowledge, this has not previously been shown for polymeric ISMs. The water uptake/release is a rather slow process taking place during several hours depending

on the membrane thickness. Due to the low sample mass and water uptake of the SR membranes, it was concluded that the water uptake can be determined more reliably with the FT-IR-ATR technique possessing high sensitivity for detecting even traces of water.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors acknowledge the Academy of Finland for financial support. Assoc. Prof. Róbert E. Gyurcsányi (Budapest University of Technology and Economics, Hungary) and Dr. Zhanna Boeva (M.V. Lomonosov Moscow State University, Russia) are gratefully acknowledged for fruitful discussions. M.Sc. Anna Packalén is acknowledged for technical assistance with the FT-IR-ATR measurements shown in Figure S-1, Supporting Information.

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