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**As featured in:**



See Takayo Moriuchi-Kawakami *et al.*, *Analyst*, 2020, **145**, 3832.



Cite this: *Analyst*, 2020, **145**, 3832

# Proton spin relaxation study with pulsed NMR on the plasticization of Na<sup>+</sup> ion-selective electrode membranes prepared from PVCs with different degrees of polymerization†

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The proton spin–spin relaxation times ( $T_2$ ) of ion-selective electrode membranes with differences in the polymerization degree of the incorporated poly(vinyl chloride) (PVC) polymers were investigated.  $T_2$  measurements were performed using Hahn-Echo, Solid-Echo and Carr–Purcell–Meiboom–Gill (CPMG) pulse sequences. Analyses of the  $T_2$  measurements by Hahn-Echo pulse sequences could realize the estimation of the homogeneity and compatibility for a series of ion-selective electrode membranes and reveal a relationship with the electromotive force (EMF) response in the low-concentration region of the Na<sup>+</sup> ions. On the other hand, the normalized derivative spectra from  $T_2$  measurements by Solid-Echo and CPMG pulse sequences could approximately visualize the degree of plasticization for such potentiometric polymeric membranes. Moreover, differences in the polymerization degrees of the incorporated PVCs were scarcely found to affect the selectivity coefficients of the Na<sup>+</sup>-ISEs based on bis(12-crown-4).

Received 23rd November 2019,  
Accepted 11th May 2020

DOI: 10.1039/c9an02355k

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## Introduction

The ion-selective electrode (ISE) method<sup>1–3</sup> for the determination of ions in human body fluids is one of the most important tools in clinical analysis. Particularly, Na<sup>+</sup>-ISEs based on bis(12-crown-4) as an ionophore<sup>4–6</sup> are well established measurement tools for human urine and blood analyses. Human body fluids are high in Na<sup>+</sup> ion concentration which plays a role in many important physiological functions. However, an excess of Na<sup>+</sup> ions can lead to the retention of water in the body, causing edema and high blood pressure. Therefore, determination of the Na<sup>+</sup> ions in human body fluids is considered vital in medical screening, requiring the widespread and routine use of Na<sup>+</sup>-ISEs. Thus, the high discrimination ability of Na<sup>+</sup> ions against K<sup>+</sup> ions is strongly desired due to the relatively high K<sup>+</sup> ion concentration in human body fluids.

Na<sup>+</sup>-ISEs based on bis(12-crown-4) are solvent polymeric membrane electrodes and the plasticized potentiometric PVC membranes are generally prepared by the dissolving of an appropriate amount of bis(12-crown-4), 2-nitrophenyl octyl ether (*o*-NPOE) as the membrane plasticizer, PVC as the polymer, and sodium borate as a salt additive.<sup>4–6</sup> The prepared potentiometric PVC membranes are homogeneous and flexible. In potentiometric polymeric membranes, bis(12-crown-4) as an ionophore mainly discriminates ions. Various bis(12-crown-3) derivatives were thus designed as an alternative ionophore to bis(12-crown-4), and the Na<sup>+</sup>-ISE based on bis(12-crown-3) showed a four-fold higher discrimination of the Na<sup>+</sup> ions against K<sup>+</sup> ions than that based on bis(12-crown-4).<sup>7</sup> The ionophores of the Na<sup>+</sup>-ISEs are immobilized into the plasticized PVC membranes. Although the incorporated PVC polymers of Na<sup>+</sup>-ISEs may also influence their ion-sensing behavior, investigations into the ion-sensing behavior of the potentiometric membranes prepared from PVCs with different degrees of polymerization have yet to be carried out. Furthermore, a suitable and valid analysis method to evaluate the differences of such potentiometric polymeric membranes has yet to be developed.

In this study, five potentiometric PVC membranes of Na<sup>+</sup>-ISEs were prepared from PVCs with different degrees of polymerization and their ion-sensing behaviors were investigated by potentiometric measurements. Due to its extensive utilization to commercial Na<sup>+</sup>-ISEs for clinical examinations,

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† Electronic supplementary information (ESI) available: Digital images, high-precision transverse magnetization data and expanded normalized derivative spectra. See DOI: 10.1039/c9an02355k



bis(12-crown-4) was chosen as the model ionophore. We have developed an evaluating method for the plasticization of such potentiometric PVC membranes and elucidated its correlation with the ion-sensing properties.  $^1\text{H}$  nuclear magnetic resonance (NMR) relaxation measurements have been applied to studies on the morphology, structures and dynamics of polymers.<sup>8–11</sup> Pulsed NMR experiments are very convenient to quickly determine the proton longitudinal (or spin–lattice) ( $T_1$ ) and transverse (of spin–spin) ( $T_2$ ) magnetization relaxation times.<sup>12</sup> In particular, the proton transverse relaxation times  $T_2$  are the most suitable tools to demonstrate differences in the physical properties such as molecular mobility.<sup>13–16</sup> We have previously demonstrated that the degree of plasticization in potentiometric polymeric membranes of  $\text{Ag}^+$ -ISEs based on 5,10,15,20-tetraphenyl porphyrin with differences in the type and weight of the membrane plasticizer is quantitatively exhibited in the  $T_2$  values of the major fractions F.<sup>17,18</sup> Here, the plasticization of the potentiometric PVC membranes of  $\text{Na}^+$ -ISEs based on bis(12-crown-4) prepared from PVCs with different degrees of polymerization is investigated with  $T_2$  measurements by applying three pulse sequences (Hahn-Echo,<sup>19</sup> Solid-Echo<sup>20</sup> and CPMG<sup>12</sup>). To the best of our knowledge, this is the first report elucidating the correlation between the ion-sensing properties and the proton transverse relaxation times  $T_2$  data for a series of ion-selective electrode membranes prepared from PVCs with different degrees of polymerization.

## Experimental

### Reagents and materials

All reagents are of best quality commercially available (higher than special grade) and used as received unless otherwise specified. The PVCs used as polymers of the potentiometric polymeric membranes for the  $\text{Na}^+$ -ISEs were the ZEST series-PVCs by Shin Dai-ichi Vinyl Corporation (Tokyo, Japan). Their degrees of polymerization ( $n$ ) were 800, 1000, 1300, 1700 and 2500 (ZEST-800Z, ZEST-1000Z, ZEST-1300Z, ZEST-1700Z and ZEST-2500Z, respectively). They are actually applied to commercial  $\text{Na}^+$ -ISEs membranes for plasma, serum and urine. The bis[(12-crown-4)methyl]-2-dodecyl-2-methylmalonate (bis(12-crown-4)) used as an ionophore, 2-nitrophenyl octyl ether (*o*-NPOE) as a membrane plasticizer and tetrakis[3,5-bis(tri-

fluoromethyl)phenyl]borate sodium salt (NaTFPB) as an anion excluder were obtained from Dojindo Laboratories Co., Ltd. (Kumamoto, Japan). Tetrahydrofuran (THF) was dried over sodium and distilled.

### Preparation of potentiometric PVC membranes for the $\text{Na}^+$ -ISEs based on bis(12-crown-4)

All of the prepared potentiometric PVC membranes were composed of PVC (28.1 wt%) as a polymer, *o*-NPOE (68.9 wt%) as a membrane plasticizer, bis(12-crown-4) (2.5 wt%) as an ionophore, and NaTFPB (0.5 wt%) as an anion excluder.<sup>21</sup> The components (282.17 mg) of a potentiometric PVC membrane were placed into a 5 mL glass tube and dissolved in *ca.* 3 mL THF. One sheet for each potentiometric polymeric membrane was obtained after evaporation of the THF for a few days. The PVCs used were ZEST-800Z (for membrane 1), ZEST-1000Z (for membrane 2), ZEST-1300Z (for membrane 3), ZEST-1700Z (for membrane 4) and ZEST-2500Z (for membrane 5). Five kinds of potentiometric polymeric membranes incorporating PVCs in different degrees of polymerization (membranes 1–5) were prepared and these were all viscoelastic sheets. Digital images of these five types of membranes are shown in Fig. S1.† One sheet for each membrane was arranged in a 10 mm diameter NMR tube (10 mm  $\phi$ ) for pulse irradiation to its center. Digital image of the NMR samples are also provided in Fig. S1.†

### $T_2$ measurements with pulsed NMR

The proton transverse magnetization relaxation time  $T_2$  measurements were carried out with a JEOL JNM-MU-25 spectrometer operating at a frequency of 25 MHz. The free induction decay (FID) signals were recorded at a probe temperature of 25 °C by applying Hahn-Echo ( $90^\circ-\tau-180^\circ$ ), Solid-Echo ( $90^\circ-\tau-90^\circ$ ) and CPMG ( $90^\circ-\tau-\{[180^\circ-2\tau]_M 180^\circ-\tau\}$ -measurement- $\tau\}_N$ ) pulse sequences. By fitting the FID signals with the Hahn-Echo pulse sequence to the Weibull function,<sup>22</sup> the  $T_2$  values and their fractions were computed. The average  $T_2$  value of the whole potentiometric polymeric membrane is calculated from the weighted sum of the  $T_2$  values (Table 1). Namely, the  $T_{2M} \times F_M + T_{2L} \times F_L$  value expresses the average  $T_2$  value of the whole potentiometric polymeric membrane. The FID signals with the Solid-Echo and CPMG pulse sequences for different relaxation time ranges were analyzed to obtain high-precision transverse magnetiza-

**Table 1** Results of proton transverse relaxation times  $T_2$  measured by pulsed NMR

Potentiometric PVC membrane	Degree of polymerization $n$	FID analyses <sup>a</sup>				Average $T_2$ (ms)
		$T_{2M}$ ( $\mu\text{s}$ )	$F_M$ (%)	$T_{2L}$ (ms)	$F_L$ (%)	
Membrane 1	800	742.88	26.2	7.25	73.8	5.55
Membrane 2	1000	204.03	9.6	4.57	90.4	4.15
Membrane 3	1300	170.54	6.5	5.07	93.5	4.75
Membrane 4	1700	356.74	27.1	8.57	72.9	6.34
Membrane 5	2500	317.18	32.4	26.77	67.6	18.2

<sup>a</sup> Estimated from FID signals obtained by the Hahn-Echo pulse sequence.





tion  $M(t)$  data from the short-time region to the long-time region.<sup>18</sup> High-precision transverse magnetization  $M(t)$  data were changed to one normalized derivative spectrum by derivative calculations with respect to the logarithmic time.<sup>23,24</sup> The FID signals of each of the PVC polymers were also measured by Solid-Echo and CPMG pulse sequences, and the normalized derivative spectra were obtained (Fig. S2 and S3†).

### EMF measurements

The potentiometric PVC membranes for the ISEs were formed on the tip of the ISE body assembly with an electrode kit (DKK Co., Ltd., Tokyo) by a casting method. The obtained  $\text{Na}^+$ -ISEs were then conditioned overnight in an aqueous 0.01 M NaCl solution. An aqueous solution of 0.01 M NaCl was employed as the internal filling solution. All test solutions were made from chloride salts without any pH-adjusting buffer reagent. EMF measurements were performed on cells of type  $\text{Ag}-\text{AgCl}|3.3 \text{ M KCl}||0.1 \text{ M CH}_3\text{COOLi}|\text{sample solution}||\text{membrane}||0.01 \text{ M NaCl}|\text{AgCl}-\text{Ag}$  using a pH/mV meter equipped with a double junction type  $\text{Ag}-\text{AgCl}$  reference electrode. The activity coefficients were calculated according to the Davies equation.<sup>25</sup> All EMF measurements of the examined  $\text{Na}^+$ -ISEs were performed at 25 °C. The EMF measurements in this work were performed by the modified classical IUPAC protocol<sup>26</sup> since this work is modelled on commercial  $\text{Na}^+$ -ISEs based on bis(12-crown-4) which generally work for serum in higher ranges. EMF measurements for the calibration curves were carried out in increasing NaCl concentrations without additional background electrolytes.<sup>26</sup> During EMF measurements for the selectivity coefficients, incremental amounts of NaCl were added to the solutions containing a constant concentration of the interfering ions as background electrolytes. The selectivity coefficients of the five  $\text{Na}^+$ -ISEs,  $K_{ij}^{\text{pot}}$ , where  $i$  is the primary ion ( $\text{Na}^+$ ) and  $j$  is the interfering ion, were determined by the fixed interference method (FIM).<sup>1,2,26</sup>

## Results and discussion

### $T_2$ measurements by applying the Hahn-Echo pulse sequence

The plasticization of a polymer by a membrane plasticizer varies as the weight ratio or the kind of membrane plasticizer employed and the polymerization degree or the kind of polymers are changed.<sup>27,28</sup> Therefore, the  $T_2$  values of the proton transverse relaxation time of the potentiometric PVC membranes are dramatically affected by the degree of polymerization for the employed PVCs since constraints on the molecular motions in the potentiometric polymeric membrane are directly influenced by their plasticization degrees. To estimate quantitatively the plasticization degree of the potentiometric PVC membranes incorporating *o*-NPOE as the membrane plasticizer, here, five kinds of potentiometric polymeric membranes made from PVCs with different degrees of polymerization were prepared (membranes 1–5). The degrees of polymerization ( $n$ ) of the PVCs for membranes 1–5 were 800, 1000, 1300, 1700 and 2500, respectively. Membranes 1–5 strongly

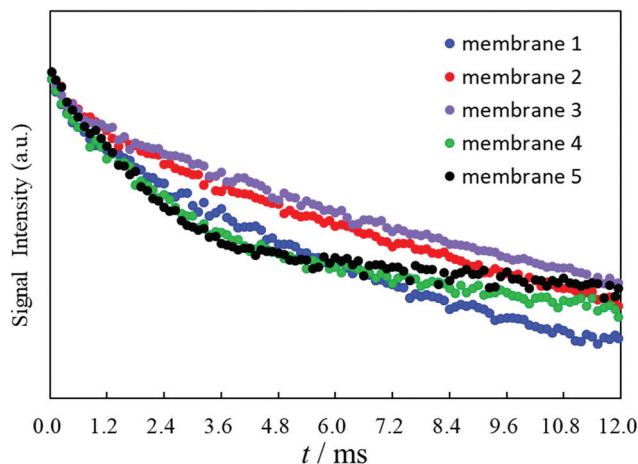


Fig. 1 FID signals with the Hahn-Echo pulse sequence of the five potentiometric polymeric membranes 1–5.

resembled each other and no differences in their digital images were observed (Fig. S1†).  $T_2$  measurements were performed using a 25 MHz pulsed NMR spectrometer. The FID signals of membranes 1–5 for calculation of the  $T_2$  values were obtained by Hahn-Echo pulse sequences (Fig. 1). Generally, Hahn-Echo pulse sequences are suitable for  $T_2$  measurements of viscoelastic samples.

The  $T_2$  values and their respective fractions  $F$ , calculated by fitting the FID signal to the Weibull function,<sup>22</sup> are summarized in Table 1. Each FID signal of the examined membranes was found to reflect two kinds of components having relaxation times  $T_{2L}$  (long) and  $T_{2M}$  (intermediate).<sup>29</sup> The longer  $T_{2L}$  and the shorter  $T_{2M}$  are attributed to mobile species such as *o*-NPOE and sluggish species such as PVCs, respectively.

The PVCs used consist of an immobile component with an extremely short  $T_2$  value<sup>29</sup> ( $T_{2S}$ ) (ca. 15  $\mu\text{s}$  by applying the Solid-Echo pulse sequence), however, precise  $T_2$  measurements could not be carried out by the Hahn-Echo pulse sequence due to their significant time consumption. The prepared potentiometric polymeric membranes incorporated 28.1 wt% PVC. In membrane 5, the incorporated polymer had the highest PVC molecular weight PVC ( $n = 2500$ ). Membrane 5 showed an incomparably long  $T_{2L}$  value (26.77 ms) with the major fraction  $F_L$  (67.6%) and a moderate  $T_{2M}$  value (317.18  $\mu\text{s}$ ) with the fraction  $F_M$  (32.4%). This means that membrane 5 consists of a highly mobile component of 67.7% and relatively immobile component of 32.4%. Since membrane 5 possessed the longest  $T_{2L}$  value and comparable amounts of the major fraction  $F_L$ , it also provided the largest average  $T_2$  value (18.2 ms). In our previous paper, the average  $T_2$  values exhibited the degree of plasticization for the potentiometric polymeric membranes.<sup>18</sup> The degree of plasticization is potentially displayed as the position, area and breadth of the normalized derivative spectra peaks. In the case of similar membranes, the average  $T_2$  values will indicate the degree of plasticization for the whole membranes since they will adapt closely with changes in the position, area and breadth of the normal-



ized derivative spectra peaks. In the case of membrane 5, its large average  $T_2$  value indicates a large degree of plasticization. Considering the fraction  $F_L$  value in Table 1, however, it seems that *o*-NPOE as a membrane plasticizer could not very well permeate the polymer chains of the incorporated PVC, leading to a worsening of the compatibility of PVC with the *o*-NPOE in membrane 5. On the other hand, membranes 2 and 3 incorporating PVCs with polymerization degrees  $n = 1000$  and  $1300$  consisted of almost all mobile components accompanied by the major fractions  $F_L$  (90.4 and 93.5%) and providing the relatively longer  $T_{2L}$  values (4.57 and 5.07 ms), respectively. These results indicate that *o*-NPOE as a membrane plasticizer could permeate the polymer chains of the incorporated PVCs well, leading to excellent homogeneity and compatibility.

Membranes 1 and 4 incorporating PVCs with polymerization degrees  $n = 800$  and  $1700$  exhibited relatively longer  $T_{2L}$  values (7.25 and 8.57 ms) with major  $F_L$  fractions (73.8 and 72.9%), respectively. Membranes 1 and 4 also possess relatively immobile components, which showed relatively shorter  $T_{2M}$  values (742.88 and 356.74  $\mu$ s) accompanied by moderate fractions  $F_M$  (26.2 and 27.1%), respectively. The average  $T_2$  value of membrane 4 (6.34 ms) was higher than that of membrane 1 (5.55 ms), while it is noteworthy that membrane 1 had the largest  $T_{2M}$  value (742.88  $\mu$ s) among the membranes 1–5. Therefore, it is presumed that the homogeneity and compatibility of membrane 1 are superior to those of membrane 4.

The plots for the polymerization degrees of the incorporated PVCs vs the average  $T_2$  values are given in Fig. 2.  $T_2$  measurements by applying the Hahn-Echo pulse sequences demonstrated that the membrane which exhibits the minimum average  $T_2$  value would be the most suitable membrane with excellent homogeneity and compatibility.

### $T_2$ measurements by applying the Solid-Echo and CPMG pulse sequences

Generally, the Solid-Echo and CPMG pulse sequences are used to obtain the FID signals for the  $T_2$  values of the solid and liquid samples, respectively. We previously demonstrated that the normalized derivative spectra acquired from  $T_2$  measure-

ments by the Solid-Echo and CPMG pulse sequences could visualize the degree of plasticization for the potentiometric PVC membranes with differences in the membrane plasticizer weight.<sup>18</sup> In order to visualize the plasticization of the potentiometric polymeric membranes 1–5 with differences in the polymerization degree of the incorporated PVC polymers, here, the normalized derivative spectra in a time range of 2.5  $\mu$ s to 20 000 000  $\mu$ s acquired by applying the Solid-Echo (2.5–140  $\mu$ s) and CPMG (140–2 000 000  $\mu$ s) pulse sequences were obtained from high-precision transverse magnetization  $M(t)$  data (Fig. 3).<sup>18</sup> Moreover, the normalized derivative spectra of the membrane plasticizer *o*-NPOE and PVC ( $n = 2500$ ) are also illustrated in Fig. 3. The scale of the horizontal axis is logarithmic.

Since the relaxation peaks of all the PVCs ( $n = 800, 1000, 1300, 1700$  and  $2500$ ) appeared only in short-time regions up to 30  $\mu$ s, the normalized derivative spectra of the PVCs themselves were very similar (Fig. S3†). Therefore, no difference in the degree of plasticization for the PVCs was observed in the normalized derivative spectra of the PVCs themselves. On the other hand, a remarkable difference between the potentiometric polymeric membranes 1–5, PVCs and *o*-NPOE was clearly observed in the normalized derivative spectra (Fig. 3). These results establish that the membrane plasticizer *o*-NPOE permeates the PVC polymer chains and the constraints on the molecular motions of PVC are dramatically reduced, while constraint on the molecular motions of *o*-NPOE are, in contrast, markedly increased.

In the normalized derivative spectra of membranes 1–5, the relaxation peaks of PVC originally in the short-time region were significantly diminished but most shifted to the wider field of the long-time regions by plasticization. The  $T_2$  relaxations of membranes 1–5 were found in a wide field of the long-time regions of 200  $\mu$ s to 250 000  $\mu$ s. The bottoms of large relaxation peaks for the investigated potentiometric polymeric membranes (excluding membrane 5) appeared at around 10 000  $\mu$ s. Although the differences between membranes 1–4 could be visualized (Fig. 3 and S4†), they were in large part in

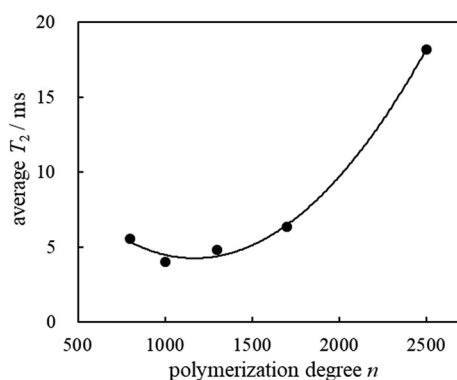


Fig. 2 Changes in the average  $T_2$  values with the polymerization degrees of the incorporated PVCs.

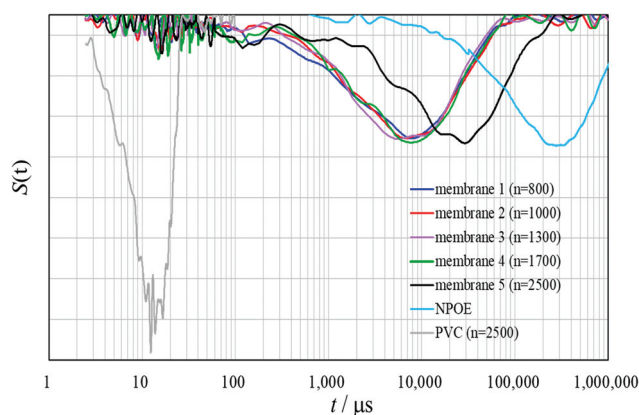


Fig. 3 Normalized derivative spectra of the potentiometric polymeric membranes 1–5.



accordance with results by the Hahn-Echo pulse sequence, as illustrated in Fig. 2. Membrane 5 exhibited a relaxation peak in the relatively longer time region than membranes 1–4 due to its largest average  $T_2$  value and this was in good accordance with results by the Hahn-Echo pulse sequences. Thus,  $T_2$  measurements by applying the Solid-Echo and CPMG pulse sequences proved that the normalized derivative spectra could approximately visualize the degree of plasticization for the potentiometric polymeric membranes with differences in the polymerization degrees of the incorporated PVC polymers. Unlike the Hahn-Echo pulse sequence, however, the small differences between membranes 1–4 could not be characterized precisely in the normalized derivative spectra (Fig. 4S†). That is, it was not possible to elucidate detailed differences between the potentiometric polymeric membranes resulting from the polymerization degree of the incorporated polymers by  $T_2$  measurements with the Solid-Echo and CPMG pulse sequences.

### Potentiometric responses

The potentiometric responses of the ion-sensing polymeric membranes were assumed to be influenced by the polymerization degree of the incorporated polymers since the  $T_2$  relaxations of the potentiometric polymeric membranes were somewhat dependent on the polymerization degree. Thus, the potentiometric responses of the  $\text{Na}^+$ -ISEs of membranes 1–5 were investigated. EMF measurements of the  $\text{Na}^+$ -ISEs based on bis(12-crown-4) as an ionophore were carried out in increasing NaCl concentrations. The activity coefficients were calculated according to the Davies equation.<sup>25</sup> The examined  $\text{Na}^+$ -ISEs based on bis(12-crown-4) as an ionophore displayed high sensitivity and fast potential response to the  $\text{Na}^+$  ion. Furthermore, all of the examined  $\text{Na}^+$ -ISEs exhibited good Nernstian responses to  $\text{Na}^+$ -activity changes, as shown in Fig. 4. The slopes and linear ranges of the calibration graph are summarized in Table 2.

The  $\text{Na}^+$ -ISE of membrane 3 responded to the  $\text{Na}^+$ -activity changes with slopes of  $59.17 \text{ mV decade}^{-1}$  over an activity range of  $10^{-3.6}$  to  $10^{-1.1} \text{ M}$  (Table 1). Fig. 4 clearly shows that the  $\text{Na}^+$ -ISE of membrane 1 showed the best EMF response under  $10^{-3.6} \text{ M}$  of the  $\text{Na}^+$  ions. The  $\text{Na}^+$ -ISE of membrane 3 provided the best Nernstian response from  $10^{-3.6} \text{ M}$  to  $10^{-1.1} \text{ M}$  and the worst EMF response under  $10^{-3.6} \text{ M}$  of the  $\text{Na}^+$  ions. As for the  $\text{Na}^+$ -ISEs of membranes 1–5, the differences resulting from the polymerization degrees of the incorporated PVCs were observed for the potential responses in the low-concentration region under  $10^{-3.6} \text{ M}$  of the  $\text{Na}^+$  ions. These results, as shown in Fig. 4, agreed to some extent with the FID signals illustrated in Fig. 1: the FID signal intensity at 12.0 ms becomes lower and the EMF response under  $10^{-3.6} \text{ M}$  of the  $\text{Na}^+$  ions is enhanced. Generally, the transverse relaxation of the proton magnetization occurs, then the FID signal intensity decreases. When the FID signal intensity at 12.0 ms is lower, the proton transverse magnetization relaxation occurs more quickly. Therefore, it was demonstrated by applying the Hahn-Echo pulse sequence that the EMF response under  $10^{-3.6} \text{ M}$  of

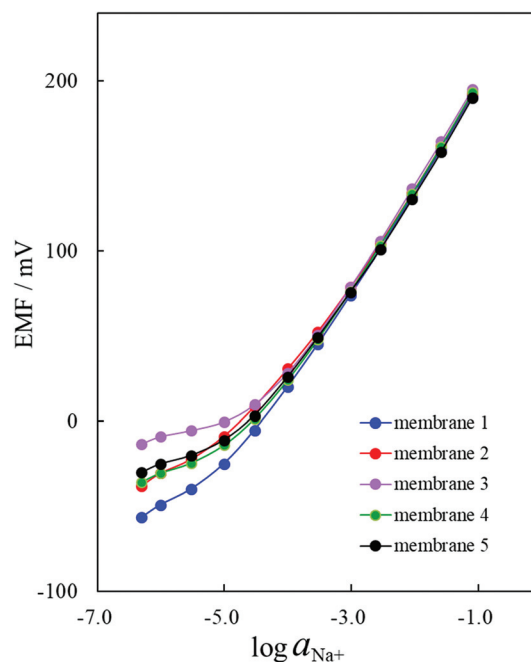


Fig. 4 EMF responses of  $\text{Na}^+$ -ISEs of membranes 1–5.

Table 2 Potential response to  $\text{Na}^+$  activity changes for the ISEs of membranes 1–5

Potentiometric PVC membrane contained in $\text{Na}^+$ -ISE	Degree of polymerization $n$	Calibration graphs	
		Slope/mV per decade	Linear range/ $\log a_{\text{Na}^+}$
Membrane 1	800	59.86	−3.71 to −1.10
Membrane 2	1000	59.15	−3.13 to −1.10
Membrane 3	1300	59.17	−3.61 to −1.10
Membrane 4	1700	59.51	−3.61 to −1.10
Membrane 5	2500	59.11	−3.13 to −1.10

the  $\text{Na}^+$  ions was enhanced when the proton transverse magnetization relaxation at 12.0 ms in the  $T_2$  measurement proceeded more greatly.

The selectivity coefficients of the  $\text{Na}^+$ -ISEs of membranes 1–5 were obtained from EMF measurements under the presence of various interfering cations. Fig. 5 illustrates the selectivity coefficients of five ISEs determined by the fixed interference method (FIM).<sup>1,2,26</sup> All of the examined ISEs exhibited good ion-selectivity for the  $\text{Na}^+$  ion, and the differences resulting from the polymerization degrees of the incorporated PVCs were negligible, as observed by their selectivity coefficients for the  $\text{Na}^+$  ions. These results are similar to those obtained showing that differences in the polymerization degrees of the incorporated PVCs were scarcely found in the Nernstian responses of the examined  $\text{Na}^+$ -ISEs. This is probably because the acquired selectivity coefficients are determined under the Nernstian responses for the  $\text{Na}^+$  ions.



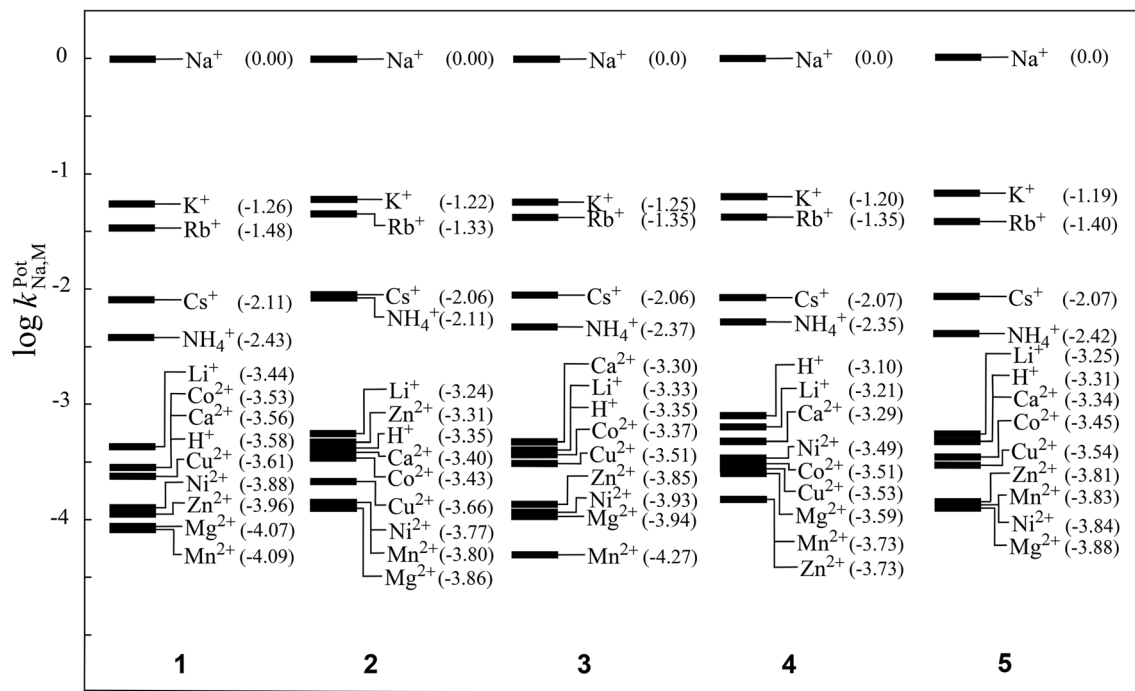


Fig. 5 Selectivity coefficients of  $\text{Na}^+$ -ISEs of membranes 1–5 determined by the fixed interference method (FIM).

## Conclusions

In summary, the proton spin-spin relaxation times ( $T_2$ ) of ion-selective electrode membranes with differences in the polymerization degrees of the incorporated PVC polymers were measured using a pulsed NMR spectrometer with Hahn-Echo, Solid-Echo and CPMG pulse sequences to acquire previously unknown information on the physical properties of ion-selective electrode membranes incorporating bis(12-crown-4) as an ionophore.  $T_2$  measurements by Hahn-Echo pulse sequence could realize the estimation of the homogeneity and compatibility of a series of ion-selective electrode membranes prepared from PVCs with different degrees of polymerization. The average  $T_2$  values calculated from  $T_2$  measurements by Hahn-Echo pulse sequence could quantify the degree of plasticization of such potentiometric polymeric membranes. Furthermore, the FID signal intensities of the  $T_2$  measurements revealed a relationship with the EMF response in the low-concentration region of the  $\text{Na}^+$  ions. Since validation checks before potentiometric measurements are a time-consuming process, data easily obtained from  $T_2$  measurements using the Hahn-Echo pulse sequence provides valuable information for the development of  $\text{Na}^+$ -ISEs. On the other hand, the normalized derivative spectra from  $T_2$  measurements by applying Solid-Echo and CPMG pulse sequences could approximately visualize the degree of plasticization for the potentiometric polymeric membranes prepared from PVCs having different degrees of polymerization. In this study, it was also found that the differences in the polymerization degrees of the incorporated PVCs scarcely affected the selectivity coefficients of the  $\text{Na}^+$ -ISEs based on bis(12-crown-4).

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This study was supported in part by a Grant-in-Aid for Scientific Research (C) (Grant No. 19K05533 to T. M-K.) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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