Potential Changes during *in situ* Formation of Carriers for Cationic Surfactant Ion-Selective Electrodes by Conditioning

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Abstract

The potential changes were monitored during symmetric conditioning and asymmetric conditioning of the polyvinyl chloride membrane containing sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) or sodium tetraphenylborate (NaTPB) in dodecyltrimethylammonium chloride (DTMACl) solutions at $10^{-5.0} - 10^{-3.5}$ mol dm^{-3}. A slow potential increase, which reflected a change in local concentration of DTMA$^+$ in the conditioning solution proximate to the membrane, was observed for NaTFPB at a DTMACl concentration of $10^{-5.0} - 10^{-4.5}$ mol dm^{-3}. For NaTFPB at a DTMACl concentration of $10^{-4.0} - 10^{-3.5}$ mol dm^{-3} or for NaTPB, the potential decreased after a rapid increase reflecting the change in DTMA$^+$:Na$^+$ ratio as a counter ion in the membrane by the ion-exchange. In asymmetric conditioning, the leakage of DTMA$^+$ into the inner solution overlapped with the change in DTMA$^+$:Na$^+$ ratio for NaTPB but was delayed from the change for NaTFPB. Some criteria for completion of the conditioning are described.

Keywords: Conditioning, Potentiometry, Quaternary ammonium salt, Surfactant ion-selective electrodes, Tetraphenylborate derivatives

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1. Introduction

Surfactant ion-selective electrodes (ISEs) have been widely used for environmental monitoring [1] and for fundamental researches [2-7].   The carriers consisting of a lipophilic cation and a lipophilic anion are usually synthesized by precipitation in an aqueous medium or by ion-pair extraction into an organic phase.   *In situ* formation is an alternative approach.   For example, an alkylammonium ISE was prepared by soaking a polyvinyl chloride (PVC) membrane containing sodium dinonylnaphthalenesulfonate and dioctyl phthalate in a $10^{-3} - 10^{-2}$ mol dm^{-3} solution of alkylammonium salt for 1 to 2 days [8].   A deteriorated tetraphenylborate (TPB$^-$) ISE based on an ion-pair of hexadecylpyridinium (HDP$^+$) and TPB$^-$ was regenerated by soaking the ISE for 1 hour successively in a 10^{-2} mol dm^{-1} NaTPB solution and in a 10^{-2} mol dm^{-3} HDPBr solution [9]; the deterioration was later overcome by introducing a more lipophilic anion like sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) [10,11].   Although such soaking for introduction of the analyte ion into the membrane phase is well known as "conditioning", its details like the appropriate concentration of the conditioning solution and the time required for conditioning have not been studied to our knowledge.

As a related research, Michalska et al. studied the depth profile of primary and interfering ions in the PVC membrane of the neutral carrier-based Pb^{2+} ISE, which was symmetrically and asymmetrically conditioned for different lengths of time [12].   In asymmetric conditioning with a 10^{-2} mol dm^{-3} Pb^{2+} solution, the diffusion of Pb^{2+} within the membrane from the conditioning solution side to the internal solution side with *o*-nitrophenyl octyl ether (*o*-NPOE) as a membrane solvent was faster than that with dioctyl sebacate (DOS).   After 1 hr, appreciable amounts of Pb^{2+} were found in the membrane phase with specific concentration profiles for both the solvents.   The profile became uniform for *o*-NPOE but remained for DOS after 20 hrs.

In the previous study, we have developed an indirect potentiometric method for anionic polyelectrolytes with a water-soluble alkylammonium ion added to the sample solution as a probe and with the ammonium ISE as a detector [13].   In order to survey the performances of a series of carriers for this purpose, we adopted *in situ* formation and eventually observed complicated potential changes during the conditioning.   In this paper, we describe the behaviors in detail and give some criteria for completion of the conditioning.

2. Experimental

NaTPB (Wako) and NaTFPB (Aldrich) were used as the salts of lipophilic anions, while dodecyltrimethylammonium chloride (DTMACl, Wako) as the salt of a lipophilic cation.   One of the resulting carriers, $(DTMA^+, TPB^-)$ was separately prepared by dropwise addition of a NaTPB solution into a DTMACl solution followed by addition of acetone; the crude material was recrystallized from acetone:ethanol (1:1).   PVC (Wako, n=1100) as the polymer matrix was purified by precipitation from a tetrahydrofuran (THF) solution with methanol.

The polymeric membrane was prepared by casting the THF solution containing 2 mg NaTFPB or 1 mg NaTPB and/or $(DTMA^+, TPB^-)$, 132 mg o-NPOE, and 66 mg PVC on a petri dish of 34-mm diameter.   After evaporation, the thickness of the membrane near the center was around 100 μm.   The central portion was cut off and fixed on a PVC tube.   The chemical amount of the lipophilic anion in a single ISE membrane was estimated to be around 0.2 – 0.3 μmol.   The internal solution consisted of a 0.05 mol dm^{-3} phosphate buffer at pH 6.8 and 0.01 mol dm^{-3} NaCl so as not to form any precipitate of potassium salts with a carrier.   The same concentrations of $DTMA^+$ salts as that of the conditioning solution were added to the internal solution for symmetric conditioning but not for asymmetric conditioning.   The ISE was conditioned in $DTMA^+$ solutions in the concentration range of $C_{DTMA} = 10^{-5.0} – 10^{-3.5}$ mol dm^{-3} with mechanically stirring at 100 rpm under the wet nitrogen atmosphere.   Since the volume of a conditioning solution was 50 cm^3, the molar ratio of $DTMA^+$ to a lipophilic anion was around 2 – 60.   The electromotive force of the cell, Ag/AgCl|NaCl(satd)|test solution|membrane|internal solution|Ag/AgCl, was measured with a potentiometer (Denki Kagaku Keiki Co., Tokyo, Japan) at 25.0±0.1°C and was recorded at the time intervals of 2 min.

3. Results and Discussion

3.1. Potential Responses of ISEs to Na^+ and $DTMA^+$

The potential responses of ISEs containing $TFPB^-$ and TPB^- salts are shown in Figs. 1(A) and 1(B), respectively.   The NaTFPB- and NaTPB-based ISEs showed Nernstian responses to Na^+ between $10^{-3.0}$-$10^{0.0}$ mol dm^{-3}.   In contrast, the $(DTMA^+, TFPB^-)$- and $(DTMA^+, TPB^-)$-based ISEs showed Nernstian responses to $DTMA^+$ between $10^{-6.0}$ – $10^{-3.0}$ mol dm^{-3}.   A series of membranes were prepared by mixing NaTPB and

separately prepared (DTMA$^+$,TPB$^-$) at different molar ratios (75:25, 50:50, 25:75) with the total amount of TPB$^-$ kept constant as mimics of the intermediate states during the conditioning, although the distribution profiles of the two components within the membrane were definitely different from each other.   The responses of the ISEs using these membranes as well as a 100:0 membrane as the initial state are also included in Fig. 1(B) [(b) – (e)].   Drifting potentials of these four ISEs were extrapolated to time zero.

   The potential of this system is governed by the concentrations of DTMA$^+$ and Na$^+$ in the inner solution, the membrane, and the outer solution.   Thus the mixed-potential theory should be applied to the two interfaces for rigorous treatment in principle [14 – 16].   DTMA$^+$ with much higher extractability than Na$^+$, however, mainly contributes to the potential, except for the extreme conditions.   Moreover, since the internal solution is not stirred, the interface between the membrane and the internal solution promptly reaches the steady state, especially for NaTFPB.   In this work, qualitative explanation was accordingly examined on the assumption that the potential in each short interval was given by the phase boundary potential between the membrane and the outer solution as expressed by eq. 1:

$$E = E^0 + 0.0592 \log ([\text{DTMA}^+]_\text{aq}/[\text{DTMA}^+]_\text{memb}) \qquad (1)$$

DTMA$^+$ interacts with TPB$^-$ in the membrane phase according to the association constant, K,

$$(\text{DTMA}^+)_\text{memb} + (\text{TPB}^-)_\text{memb} = (\text{DTMA}^+,\text{TPB}^-)_\text{memb} \qquad (2)$$
$$K=[\text{DTMA}^+,\text{TPB}^-]_\text{memb}/([\text{DTMA}^+]_\text{memb}\times[\text{TPB}^-]_\text{memb}) \qquad (3)$$

Then, the potential is given by,

$$E = E^{0'} + 0.0592 \log [\text{DTMA}^+]_\text{aq} \qquad (4)$$
$$E^{0'} = E^0 + 0.0592 \log (K\times[\text{TPB}^-]_\text{memb}/[\text{DTMA}^+,\text{TPB}^-]_\text{memb}) \qquad (5)$$

Thus, the intercept of the Nernstian response to DTMA$^+$, $E^{0'}$ would be larger at the lower [DTMA$^+$,TPB$^-$]$_\text{memb}$.   Figure 1(B) [(b) – (f)] actually shows that the membrane containing the less (DTMA$^+$,TPB$^-$) had the higher potential of the Nernstian response region.   The calibration curves were linear down to $10^{-6.0}$ mol dm^{-3} for the membranes of 0:100 and 25:75; completion of conditioning was not always necessary to obtain the

Nernstian responses. For the membranes of 50:50 and 75:25, in contrast, the super Nernstian responses were observed between $10^{-6.0}$ and $10^{-5.0}$ mol dm^{-3}. DTMA$^+$ proximate to the membrane was rapidly picked up by ion-exchange of Na$^+$, while its diffusion from the bulk to the interface was insufficient at a lower concentration of 10^{-6} mol dm^{-3} [17 – 19]. Under such conditions, the potential became lower due to reduction of the second term of eq. 4, in spite of the large $E^{0'}$. The super Nernstian response was observed between such concentrations that had a change of the determinant of the potential from one term to the other term of eq. 4.

When the same concentration of DTMA$^+$ was placed as the sample and the inner solutions of the fully conditioned ISEs, the balanced potentials were around 115 mV for (DTMA$^+$,TFPB$^-$)-based ISE and 95 mV for (DTMA$^+$,TPB$^-$)-based ISE. The higher concentration of DTMA$^+$ in the inner solution proximate to the (DTMA$^+$,TPB$^-$) membrane gave the lower potential.

3.2. Symmetric Conditioning

The potential changes during symmetric conditioning of NaTFPB- and NaTPB-based electrodes at $C_{\text{DTMA}} = 10^{-5.0} - 10^{-3.5}$ mol dm^{-3} are shown in Figs. 2(A) and 2(B), respectively. The time course was monitored at least three times at each C_{DTMA}. Although the time scale was not highly reproducible ($\pm 20\%$), the overall feature was maintained. In principle, while the transport of DTMA$^+$ through the membrane is absent, the ion-exchange of Na$^+$ with DTMA$^+$ proceeds on both sides of the membrane.

With use of NaTFPB at $C_{\text{DTMA}} = 10^{-5.0} - 10^{-4.5}$ mol dm^{-3} (Fig. 2(A)), the DTMA$^+$ concentration of the conditioning solution proximate to the membrane was kept low in the initial stage to give the lower potentials, because of the high ion-pair extracting ability of TFPB$^-$ and of the rapid uptake of DTMA$^+$ relative to the diffusion from the bulk. In the final stage of ion-exchange, the DTMA$^+$ concentration proximate to the membrane surface increased to that of the bulk and gave steady potential around 120 mV close to the balanced potential mentioned above. Although the [TFPB$^-$]$_{\text{memb}}$/[DTMA$^+$,TFPB$^-$]$_{\text{memb}}$ ratio in the second term of eq. 5 should have a decrease by the progress of the cation-exchange of NaTFPB giving (DTMA$^+$,TFPB$^-$), the potential virtually reflected the second term of eq. 4. Since the rate of conditioning was controlled by the diffusion of DTMA$^+$ in an aqueous solution, the conditioning time increased with a decrease in C_{DTMA} (70 min at $C_{\text{DTMA}} = 10^{-4.5}$ mol dm^{-3} and 210 min at $C_{\text{DTMA}} = 10^{-5.0}$ mol dm^{-3}). At the higher concentration of $C_{\text{DTMA}} = 10^{-4.0} - 10^{-3.5}$ mol dm^{-3}, the ISE responded to DTMA$^+$ reaching the membrane surface without appreciable

loss by uptake to give extraordinary high potentials, due to the large second term of eq. 5 in the initial stage.   The progress of the cation-exchange reduced the ratio and thereby decreased the potential response.   The ISE-1, conditioning of which by $10^{-4.0}$ mol dm^{-3} DTMA$^+$ solution was interrupted at a potential around 120 mV, showed substantially the same response as the membrane 0:100.   Thus, leveling the potential may be a sign for completion of the conditioning.

   With use of NaTPB, the DTMA$^+$ concentration in the conditioning solution proximate to the membrane did not decrease so much in the initial stage even at C_{DTMA} = $10^{-5.0}$ mol dm^{-3}.   The behaviors resembled to those in the NaTFPB system at C_{DTMA} = $10^{-4.0}$ – $10^{-3.5}$.   The potential became steady after 400 min at C_{DTMA} = $10^{-4.5}$ mol dm^{-3} and after 1000 min at C_{DTMA} = $10^{-5.0}$ mol dm^{-3}.   The longer time required for completion of the conditioning of NaTPB than that of NaTFPB may be attributed to the less extracting ability.   This may also induce the leakage of NaTPB into the conditioning and internal solutions [11] followed by the ion-pair extraction as (DTMA$^+$,TPB$^-$).

3.3. Asymmetric Conditioning

   The potential changes during asymmetric conditioning of NaTFPB- and NaTPB-based electrodes at C_{DTMA} = $10^{-5.0}$ – $10^{-3.5}$ mol dm^{-3} are shown in Figs. 3(A) and 3(B), respectively.   The potentials in NaTFPB and NaTPB extrapolated to time zero are given in Figs. 1(A) and 1(B) as (b), respectively.   In addition to the ion-exchange, the transport of DTMA$^+$ from the conditioning solution to the internal solution is expected in this system for the longer time scale as well.

   The potential changes in NaTFPB at C_{DTMA} = $10^{-5.0}$ – $10^{-4.5}$ mol dm^{-3} resembled to those in symmetric conditioning except for a small decrease observed after an increase. This is attributed to the start of leakage of DTMA$^+$ from the membrane into the internal solution by the ion-exchange with Na$^+$.   After the decrease, the potential became constant, which reflected C_{DTMA}.   This was because the leakage immediately reached the steady state, due to the high extracting ability of TFPB$^-$.   Potential responses were examined for the two ISEs, conditioning of which at C_{DTMA} = $10^{-5.0}$ mol dm^{-3} was interrupted at a potential around 90 mV (ISE-2) and at a peak potential (ISE-3).   The ISE-2 showed a super Nernstian response due to the remaining NaTFPB, while the ISE-3 showed substantially the same response as the membrane 0:100.   Thus, the appearance of the decrease may be the sign for completion of the conditioning in the NaTFPB system.   A similar decrease expected at the higher C_{DTMA} = $10^{-4.0}$ – $10^{-3.5}$ mol

dm^{-3} was not differentiated from the preceding potential decrease due to a change of the second term of eq. 5.   A further decrease down to the balanced potential was too slow to be recognized.

   After   the NaTFPB membrane conditioned with $10^{-4.5}$ mol dm^{-3} DTMA$^+$ solution (2500 min) reached the steady potential, the DTMA$^+$ concentration in the internal solution was determined to be $10^{-5.2}$ mol dm^{-3} by ion-pair extraction with picrate.   An appreciable amount (around 20%) of DTMA$^+$ was transported into the inner solution, although complete equilibration was not achieved.

   In the NaTPB system, the small decrease was also observed at $C_{DTMA} = 10^{-5.0} – 10^{-4.5}$ mol dm^{-3}.   The potentials in the NaTPB system were, however, much higher than those in the NaTFPB system and kept decreasing for as long as 10 days.   This is ascribed to the leakage of NaTPB into the conditioning and inner solutions as described in 3.2 and to the start of the leakage of DTMA$^+$ from the membrane into the inner solution before completion of the ion-exchange.   The potential responses were examined for the two ISEs, conditioning of which at $C_{DTMA} = 10^{-4.5}$ mol dm^{-3} was interrupted before and after the decrease (ISE-4 and 5).   The ISE-4 showed a super Nernstian response resembling to the calibration curve with the membrane 50:50, while the ISE-5 showed a response resembling to the membrane 25:75.   Thus, the small decrease may not be the sign for completion of the conditioning in the NaTPB system.

4. Conclusions

   The potential changes were monitored during symmetric conditioning and asymmetric conditioning of the PVC membrane containing NaTPB or NaTFPB in DTMACl solutions at $10^{-5.0} – 10^{-3.5}$ mol dm^{-3}.   In order to obtain the Nernstian response, 200 min was enough in asymmetric conditioning at $C_{DTMA} >10^{-4.0}$ mol dm^{-3}. After 200 min, the potential became constant in NaTFPB, while being higher and continuously decreasing in NaTPB.   The slow decrease in NaTPB is due to the leakage of NaTPB into the inner solution followed by the ion-pair extraction as (DTMA$^+$,TPB$^-$) with DTMA$^+$ transported into the inner solution.   In symmetric conditioning, the potential change was simplified in the absence of leakage into the inner solution.   A small decrease in potential in the asymmetric conditioning at the relatively low DTMA$^+$ concentration or the potential leveling in the symmetric conditioning may be a sign of completion for NaTFPB but not for NaTPB.

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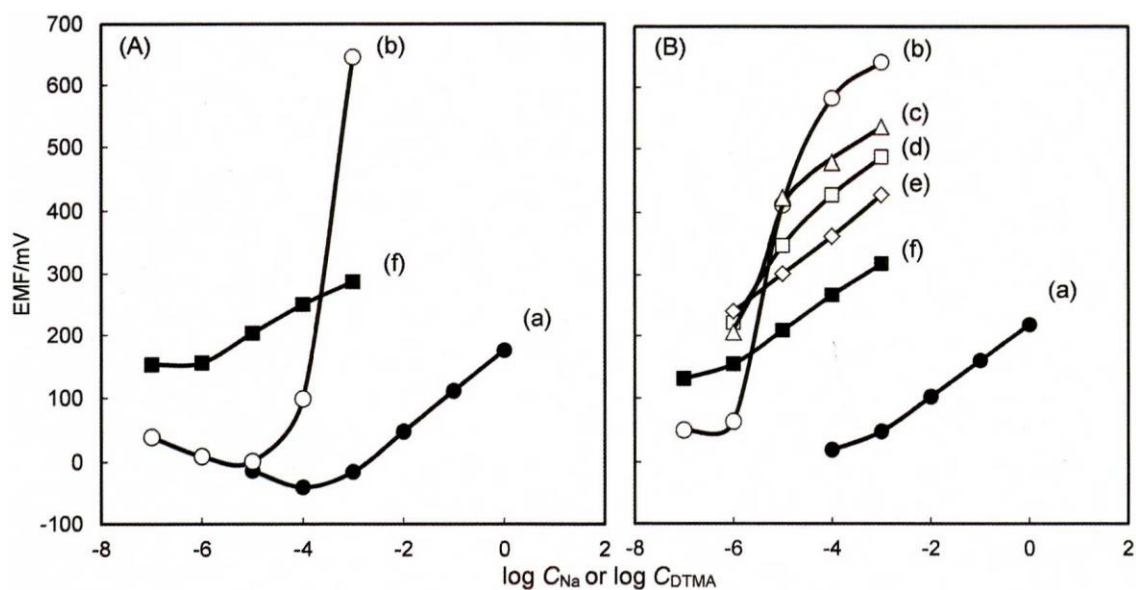[19] T. Sokalski, A. Ceresa, M. Fibbioli, T. Zwickl, E. Bakker, E. Presch, *Anal. Chem.* 71 (1999) 1210.

Fig. 1. Potential responses of ISEs based on TFPB$^-$ (A) and TPB$^-$ (B) salts to Na$^+$ (a) and DTMA$^+$ (b-f) ions. Na$^+$ salt:DTMA$^+$ salt ratio in PVC membrane: (a,b) 100:0 (c) 75:25 (d) 50:50 (e) 25:75 (f) 0:100. Inner solution: 0.01 mol dm^{-3} NaCl. The potentials for (b)-(e) were obtained by extrapolating the changes to time zero.
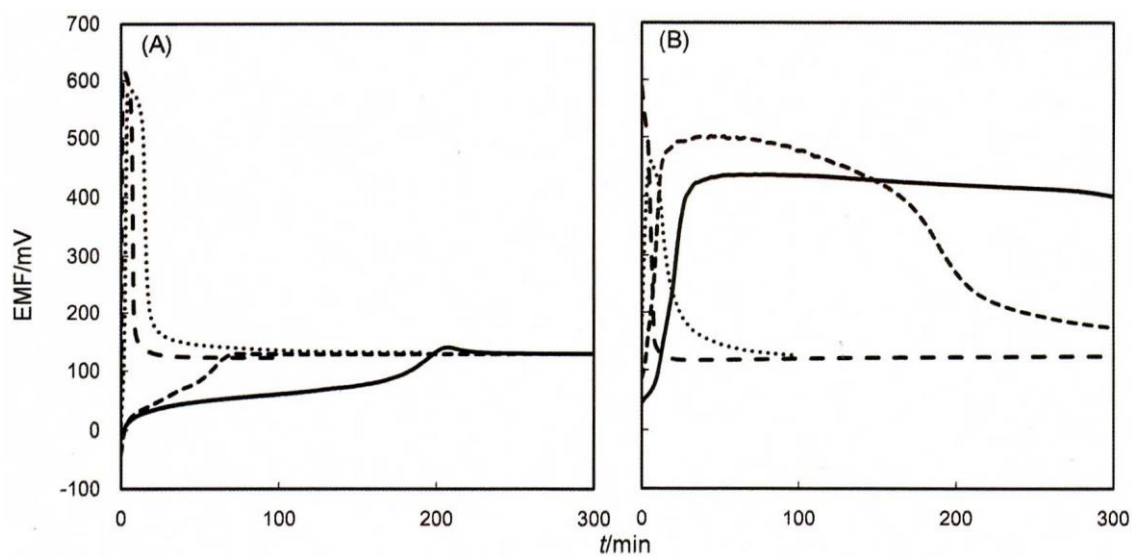
Fig. 2. Potential changes in symmetric conditioning of ISEs based on NaTFPB (A) and NaTPB (B) by DTMACl solutions. C_{DTMA}/mol dm^{-3}: (———) $10^{-5.0}$, (-----) $10^{-4.5}$, (·········) $10^{-4.0}$, (– – –) $10^{-3.5}$.
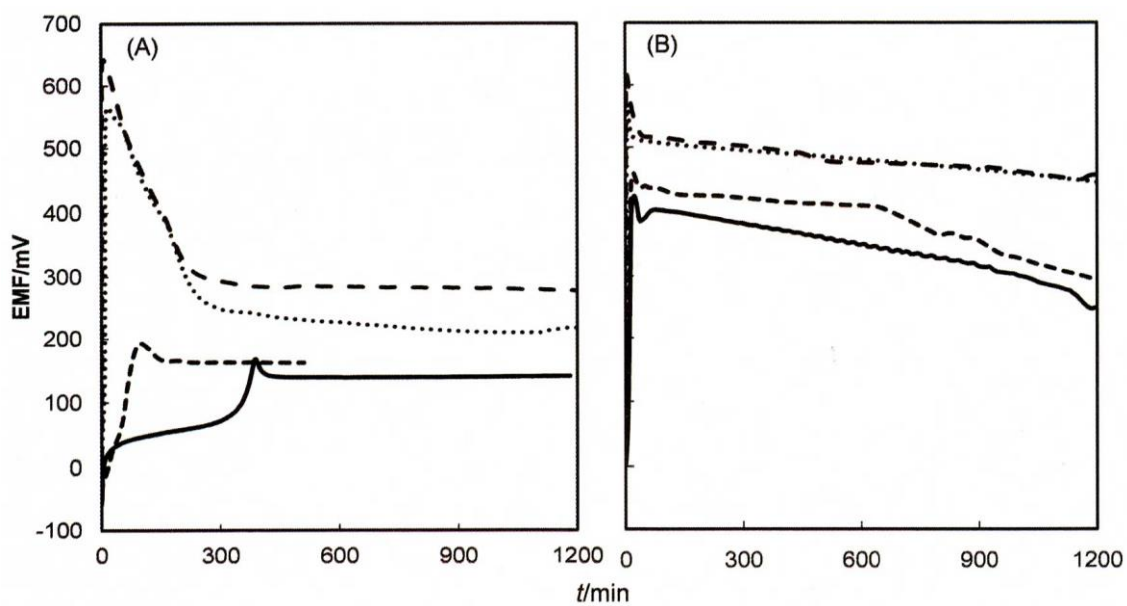
Fig. 3. Potential changes in asymmetric conditioning of ISEs based on NaTFPB (A) and NaTPB (B) by DTMACl solutions of varying concentrations. $C_{DTMA}/\text{mol dm}^{-3}$: (——) $10^{-5.0}$, (----·) $10^{-4.5}$, (········) $10^{-4.0}$, (– – –) $10^{-3.5}$.