Effect of Surfactants on the Electrochemical Performance of Cation-Selective Membrane Electrodes

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We examined the effect of polyether-type nonionic surfactants (Brij 35, Triton X-100, Tween 20 and Tween 80) on the potentiometric properties of sodium-, potassium- and calcium-selective membranes which are prepared with widely used ionophores and four kinds of polymer matrices [poly(vinyl chloride) (PVC), polyurethane (PU), PVC/PU blend, and silicone rubber (SR)]. It was found that the PVC-based membranes, which provide the best performance among all other matrix-based membranes in the absence of nonionic surfactants, exhibited larger change in their potentiometric properties when nonionic surfactants are added to the sample solution. On the other hand, the sodium-selective SR-based membrane with calix[4]arene, potassium-selective PVC/PU- or SR-based membrane with valinomycin, and the calcium-selective SR-based membrane with ETH 1001 provide almost identical analytical performance in the presence and absence of Tween 20 or Tween 80 surfactants. The origin of nonionic surfactants effect was also investigated by interpreting the experimental results obtained with various matrices and ionophores. The results suggest that the nonionic surfactant extracted into the membrane phase unselectively form complexes with the primary and interfering ions, resulting in increased background potential and lower binding ability for the ionophore. Such effects should result in deteriorated detection limits, reduced response slopes and lower selectivity for the primary ions.

Key Words : Nonionic surfactant, Ion-selective electrode, Polymer matrix, Triton X-100

Introduction

Ion-selective electrodes (ISEs), especially those with neutral carrier-based solvent polymeric membranes, have been studied for more than three decades, and are now routinely employed for direct potentiometric measurements of various ionic species in environmental, industrial and clinical samples.[1,2] For example, many automated commercial blood gas/electrolyte analyzers employ polymer membrane-based ISEs as their primary detectors. Such systems commonly operate with calibration and washing solutions that contain nonionic surfactants which are added to enhance cleaning efficiency and to prevent entrapment of air bubbles in the flow channels.[3]

Both ionic and nonionic surfactants may interact with and partition into the solvent polymeric membranes.[3] In fact, solvent polymeric membranes containing anionic (e.g., tetrakis-phenylborates) or cationic (quaternary alkylammoniums) sites have long been used for the measurement of cationic and anionic surfactants.[4,5] Although neutral nonionic surfactants may not cause a large response in themselves, it is predicted that their presence in sample solutions may bring about interfering responses in the determination of other ionic species (e.g., Na^+, K^-, Ca^{2+}, etc.) due to their substantial partitioning to the membrane phase. It was reported that poly(ethylene oxide)-based nonionic surfactants can interfere with the potentiometric response of poly(vinyl chloride) (PVC) membrane-based cation-selective membranes, resulting in significant errors in the measurement of alkali and alkaline earth metal cations.[3,6-9] However, the effects of nonionic surfactants on the EMF responses of ISEs based on various polymer matrices other than PVC have not been documented yet.
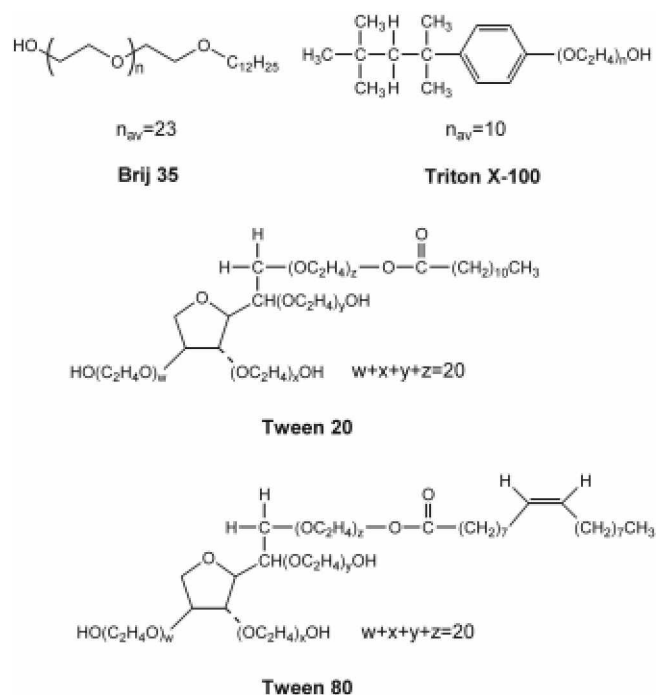

Figure 1. Structures of nonionic surfactants used in this study.

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Herein, we report the influences of various nonionic surfactants (Brij 35, Triton X-100, Tween 20 and 80; see Figure 1) on the EMF response of sodium-, potassium-, and calcium-selective membranes prepared with several different kinds of neutral carriers and polymer matrices [PVC, PU (polyurethane) and silicone rubber (SR)]. It was observed that cation-selective membrane electrodes exhibit varying degree of interfering responses to their primary ions in the presence of nonionic surfactants depending on the type of membrane formulations and ionophores incorporated. It was also found that the EMF responses of solvent polymeric cation-selective membranes significantly vary depending on the type of nonionic surfactants.

Experimental Section

Reagents. Poly(vinyl chloride) (PVC), N,N,N',N'-tetra-

cyclohexyl-1,2-phenylenedioxyldiacetamide (ETH 2120), bis[(12crown-4)methyl]dodecylmethylmalonate (Sodium VI), 4-tert-butylcalix[4]arene-tetraacetic acid tetraethylester (calix[4]arene ester), (-)-R,R-N,N'-(bis(11-ethoxycarbonyl)undecyl)-N,N'-4,5-tetramethyl-3,6-dioxaoctanediamide (ETH 1001), potassium tetrakis(4-chlorophenyl)borate (KT*p*ClPB), potassium tetrakis[3,5-bis(trifluoromethyl) phenyl]borate (KTFPB), tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500), bis(2-ethylhexyl)adipate (DOA), bis(2-ethylhexyl)sebacate (DOS), 2-nitrophenyl octyl ether (NPOE) were purchased from Fluka Chemie AG (Buch, Switzerland). Monensin methyl ester (MME) was obtained from Calbiochem-Novabiochem (La Jolla, CA, USA). Valinomycin, poly(ethylene glycol)monolauryl ether (Brij 35), poly(ethylene glycol)*p*-isooctylphenyl ether (Triton X-100), polyoxyethylene sorbitol monolaurate (Tween 20), polyoxyethylene sorbitol monooleate (Tween

Table 1. Compositions of the sodium-selective membranes[a]

No.	Matrix			Ionophore				Additive		Plasticizer		
	PVC[b]	PU[c]	SR[d]	MME[e]	Calix[4]arene[f]	ETH 2120[g]	Sodium VI[h]	KTpClPB[i]	KTFPB[j]	DOA[k]	DOS[l]	NPOE[m]
1	32.9			1.0				0.3				65.8
2	8.2	24.7		1.0				0.3				65.8
3		32.9		1.0				0.3				65.8
4			77.5	0.8						21.7		
5	32.9				1.0			0.3			65.8	
6	8.2	24.7			1.0						65.8	
7		32.9			1.0						65.8	
8			98.5		1.0				0.5			
9	33					1.0				66.0		
10	8.3	24.7				1.0				66.0		
11		33.0				1.0				66.0		
12			77.5			1.0				21.7		
13	33						1.0					66.0
14	8.3	24.7					1.0					66.0
15		33.0					1.0					66.0
16			77.5				1.0			21.7		

[a]In wt%. [b]High-molecular-weight poly(vinyl chloride). [c]Tecoflex polyurethane. [d]3140RTV silicone-rubber. [e]Monensin methyl ester. [f]4-tert-butyl calix[4]arene-tetraacetic acid tetraethylester. [g]N,N,N',N'-tetracyclohexyl-1,2-phenylenedioxyldiacetamide. [h]Bis[(12crown-4)methyl]dodecylmethyl-malonate. [i]Potassium tetrakis(4-chlorophenyl) borate. [j]Potassium tetrakis[3,5-bis(trifluoromethyl) phenyl]borate. [k]Bis(2-ethylhexyl)adipate. [l]Bis(2-ethylhexyl)sebacate. [m]2-nitrophenyl octyl ether.

Table 2. Compositions of the potassium- and calcium-selective membranes[a]

No.	Matrix			Ionophore		Additive		Plasticizer	
	PVC[b]	PU[c]	SR[d]	Valinomycin	ETH 1001[e]	KTpClPB[f]	ETH 500[g]	DOA[h]	DOS[i]
17	33.0			1.0				66.0	
18	8.3	24.7		1.0				66.0	
19		33.0		1.0				66.0	
20			77.5	0.8				21.7	
21	32.9				1.0				65.8
22	8.2	24.7			1.0				65.8
23		32.9			1.0				65.8
24			77.5		1.0	0.2	0.3	21.7	

[a]In wt%. [b]High-molecular-weight poly(vinyl chloride). [c]Tecoflex polyurethane. [d]3140RTV silicone-rubber. [e](-)-R,R-N,N'-(bis(11-ethoxycarbonyl)-undecyl)-N,N'-4,5-tetramethyl-3,6-dioxaoctanediamide. [f]Potassium tetrakis(4-chlorophenyl)borate. [g]Tetradodecylammonium tetrakis(4-chlorophenyl)-borate. [h]Bis(2-ethylhexyl)adipate. [i]Bis(2-ethylhexyl)sebacate.

80), tris-(hydroxymethyl)aminomethane were obtained from Sigma Chemical Co. (St. Louis. MO. USA). 3140 RTV silicone rubber (SR) was a product of DOW Corning Co. (Midland. MI. USA), and Tecoflex SG-80A polyurethane from Thermedics (Midland. MI). All other chemicals used were analytical-reagent grade. Standard solution and buffer were prepared with deionized water (18 MW cm).

Preparation of Ion-Selective Membranes. PVC- and polyurethane (PU)-based membranes were prepared with 1 wt% ionophore. 32.9-33 wt% matrices (PVC. PVC/PU. PU). 66 wt% plasticizer and lipophilic additive (if necessary). These membrane components dissolved in 1 mL THF were then poured into a glass ring (i.d. 22 mm) placed on a slide glass. and dried overnight at room temperature. SR-based membranes were fabricated by dissolving 77.5-98.5 wt% SR. 1-0.8 wt% ionophore. 21.7-0 wt% plasticizer and appropriate amounts of lipophilic additive in 0.4 mL THF and by casting the mixture in a glass ring (i.d. 22 mm) placed on a flat Teflon plate. and dried for 3-5 days at room temperature. Table 1 and 2 summarize the compositions of cation-selective polymer membranes examined in this study.

Evaluation of Polymer Membranes. Small disk (5.5 mm) were punched from cast films and mounted in Phillips electrode bodies (IS-561; Glasblaserei Moller. Zurich. Switzland). The internal filling solution were 0.1 M NaCl for Na$^+$-. 0.1 M KCl for K$^-$-. and 0.1 M CaCl$_2$ for Ca^{2+}-selective electrodes. An Orion sleeve-type double junction Ag/AgCl electrode (Model 90-02) was used as the external reference. Potential difference between the ISEs and the reference electrode was measured using an IBM AT-type computer equipped with a home made high-impedance input 16-channel analog-to-digital converter. The potentiometric behaviors were obtained by adding standard solution to 200 mL of magnetically stirred background electrolyte [0.05 M Tris-HCl. pH 7.2 or 0.05 M Tris-HCl. pH 7.2. containing various nonionic surfactants (0.05 wt%)] every 100 s to vary the concentrations of primary ions stepwise from 10^{-6} to 10^{-1} M. and the measurements of EMF values were taken every second at room temperature. Selectivity coefficients were estimated according to the separate solution-matched potential method (IUPAC SSM II method).[10]

Results and Discussion

Effect on the Sodium-Selective Electrodes. Sodium-selective membranes were prepared with various polymer matrices (PVC. PVC/PU. PU and SR) employing four kinds of sodium-selective ionophores (MME. calix[4]arene ester. ETH 2120 and Sodium VI) to see if the effect of nonionic surfactants are dependent on the type of matrices and/or neutral carriers.

Table 3 summarizes the potentiometric response curves of the MME-based sodium-selective electrodes to varying Na$^+$ concentration in 0.05 M Tris-HCl buffer (pH 7.2) and the same background electrolyte with additional nonionic surfactants (0.05 wt %). The presence of nonionic surfactant in sample phase not only shifted the background potentials of

Table 3. Potentiometric properties of the MME-based sodium-selective membranes in the absence and presence of nonionic surfactants

Matrix (No.)	condition	detection limit^a	slope^b	log$K_{Na,j}^{pot}$ ^{c}	
				K$^-$	Ca^{2-}
PVC (1)	no surfactant	-5.4	59.2	-0.76	-3.39
	Brij 35^d	-4.4	53.1	0.71	-1.56
	Triton X-100^e	-4.3	50.9	1.26	-1.66
	Tween 20^f	-4.6	54.2	0.47	-1.68
	Tween 80^g	-4.8	56.0	0.07	-1.82
PVC/PU (2)	no surfactant	-4.4	54.0	-0.55	-2.66
	Brij 35	-4.2	51.3	0.61	-1.46
	Triton X-100	-4.1	46.9	1.16	-1.65
	Tween 20	-4.3	51.4	0.34	-1.62
	Tween 80	-4.3	52.9	0	-1.87
PU (3)	no surfactant	-4.3	52.9	-0.51	-2.59
	Brij 35	-4.2	51.8	0.56	-1.46
	Triton X-100	-4.1	46.2	1.13	-1.62
	Tween 20	-4.2	50.8	0.33	-1.59
	Tween 80	-4.3	51.6	0.04	-1.83
SR (4)	no surfactant	-4.0	41.9	1.76	-0.87
	Brij 35	-4.0	42.5	1.89	-0.92
	Triton X-100	-4.0	45.8	1.54	-1.62
	Tween 20	-4.0	42.2	1.70	-1.14
	Tween 80	-4.1	42.1	1.49	-1.10

^{a}log[Na$^-$]. ^{b}Response slopes in mV/decade with respect to [Na$^+$] (range: 10^{-4}-10^{-1} M). ^{c}Potentiometric selectivity coefficient were determined according to the separate solution-matched potential method (IUPAC SSM II method). ^{d}0.05 wt% Brij 35, ^{e}0.05 wt% Triton X-100, ^{f}0.05 wt% Tween 20. ^{g}0.05 wt% Tween 80.

the electrodes but also significantly changed their potentiometric properties such as detection limits. response slopes. and selectivities. The effect was most notable with the PVC-based membranes: the detection limits were deteriorated by about an order of magnitude and their sodium selectivity over potassium was reversed. On the other hand. the detection limits of PVC/PU-. PU- and SR-based membranes. which were about 10-fold higher than PVC-based one in the absence of surfactants. were much less affected by adding nonionic surfactants. Other surfactants also made the sodium-selective membranes into potassium-selective ones.

The results summarized in Table 3 clearly show that the extents of surfactant effect are largely dependent on the type of nonionic surfactant present in sample solutions. The potentiometric properties of MME-based sodium-selective membranes were most significantly altered by the presence of Triton X-100 and least by Tween 80. Nonionic surfactants comprising a non-cyclic poly(ethylene oxide) chain are known to form cationic complexes with alkali and alkaline earth metal ions.[11] The complexes may be extracted into the organic membrane phase. and tend to form ion pairs with anionic lipophilic additive which is an important component of cation-selective membranes. Hence. nonionic surfactant-cation complex extracted into the membrane can change the host-guest chemistry occurring in the membrane phase. resulting in the decreased primary ion selectivity of the
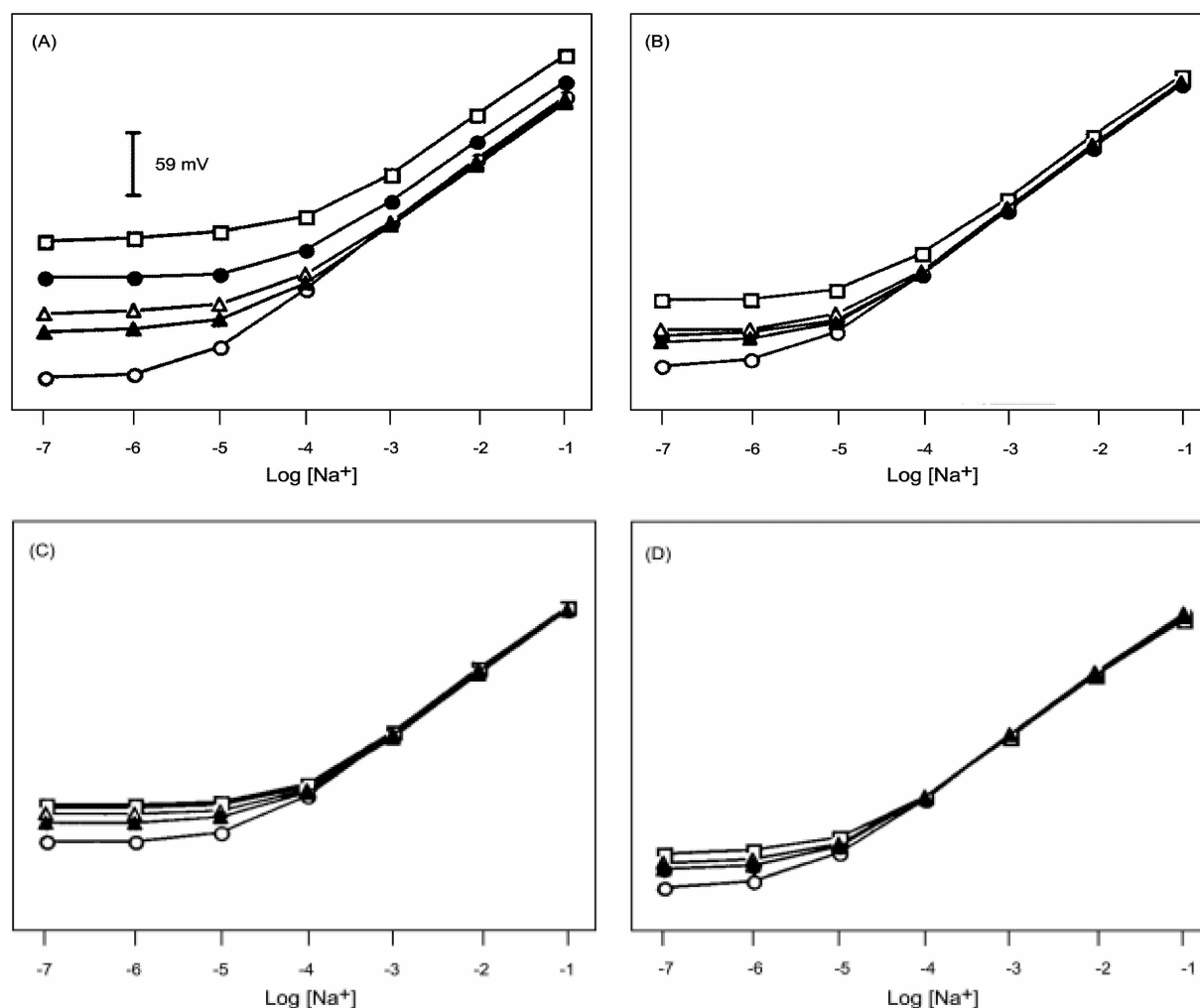
Figure 2. Potentiometric response curves of the sodium-selective electrodes based on PVC membranes with (A) monensin methyl ester (MME). (B) 4-tert-butylcalix[4]arene tetraacetic acid tetraethylester (calix[4]arene ester). (C) N,N,N',N'-tetracyclohexyl-1,2-phenyl-enedioxyldiacetamide (ETH 2120), and (D) bis[12crown-4|methyl] dodecylmethylmalonate (Sodium VI) in the absence of surfactant (○) and presence of 0.05 wt % Brij 35 (●), Triton X-100 (⬚), Tween 20 (△) and Tween 80 (▲). Background electrolyte: 0.05 M Tris-HCl buffer (pH 7.2).

membrane or even compete against the neutral carrier doped in the membrane.[3] Triton X-100, having lipophilic aromatic functional group, seems to have a larger partition constant to organic membrane phase than other nonionic surfactants, resulting in larger background EMF shifts, reduced response slopes, and reversed sodium-potassium selectivity.

The results represented in Table 3 tell us that the use of surfactants is not recommended for the MME-based sodium-selective membranes. However, the use of surfactants is unavoidable for most biomedical application of ISEs. Thus, there are certain demands for sodium-selective membranes that exhibit least surfactant effect. In search of such electrode system, we prepared twelve additional membranes employing four different polymer matrices and three kinds of sodium-selective neutral carriers, calix[4]arene, ETH 2120, and Sodium VI, which are known to form stronger sodium complexes than MME.[12] and examined their potentiometric properties. Figure 3 shows the potentiometric response curves of the PVC-based membranes prepared with those
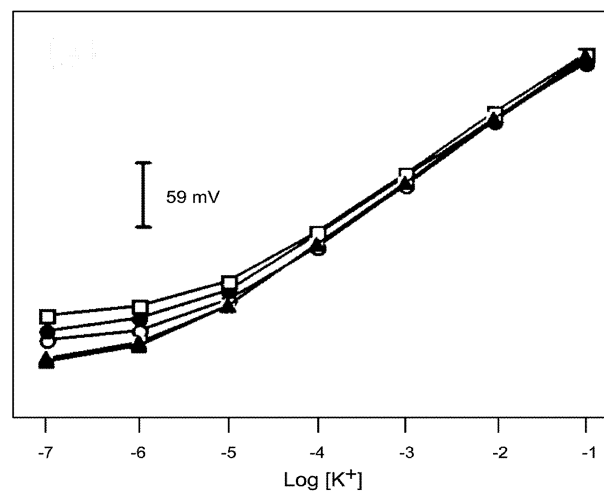

Figure 3. Potentiometric response curves of the potassium-selective electrode based on polyurethane (PU) and valinomycin in the absence of surfactant (○) and presence of 0.05 wt % Brij 35 (●), Triton X-100 (⬚), Tween 20 (△) and Tween 80 (▲).

Table 4. Potentiometric properties of the calix[4]arene-based sodium-selective membranes in the absence and presence of nonionic surfactants

Matrix (No.)	condition	detection limit[a]	slope[b]	$\log K^{pot\ c}_{Na,J}$	
				K$^+$	Ca^{2+}
PVC	no surfactant	-5.2	58.8	-2.62	-4.75
(5)	Brij 35[d]	-4.6	59.0	-1.45	-3.47
	Triton X-100[e]	-4.2	56.0	-0.35	-3.61
	Tween 20[f]	-4.5	59.0	-1.57	-3.64
	Tween 80[g]	-4.7	59.3	-1.79	-3.73
PVC/PU	no surfactant	-4.0	60.0	-2.24	-3.13
(6)	Brij 35	-4.1	58.9	-1.41	-2.83
	Triton X-100	-4.0	53.3	-0.20	-2.55
	Tween 20	-4.1	59.2	-1.72	-2.97
	Tween 80	-4.2	59.7	-1.86	-3.02
PU	no surfactant	-3.9	58.8	-2.23	-2.97
(7)	Brij 35	-4.0	57.7	-1.35	-2.67
	Triton X-100	-3.9	51.3	-0.14	-2.17
	Tween 20	-4.1	58.4	-1.75	-2.84
	Tween 80	-4.1	59.1	-1.91	-2.90
SR	no surfactant	-5.6	59.5	-2.62	-4.18
(8)	Brij 35	-5.0	57.7	-2.20	-4.46
	Triton X-100	-4.7	51.9	-1.47	-3.01
	Tween 20	-4.9	57.2	-2.30	-3.66
	Tween 80	-4.7	56.4	-2.38	-4.62

[a]log[Na$^+$]. [b]Response slopes in mV/decade with respect to [Na$^+$] (range: 10^{-4}-10^{-1} M). [c]Potentiometric selectivity coefficient were determined according to the separate solution-matched potential method (IUPAC SSM II method). [d]0.05 wt% Brij 35. [e]0.05 wt% Triton X-100. [f]0.05 wt% Tween 20. [g]0.05 wt% Tween 80.

Table 5. Potentiometric properties of the ETH 2120-based sodium-selective membranes in the absence and presence of nonionic surfactants

Matrix (No.)	condition	detection limit[a]	slope[b]	$\log K^{pot\ c}_{Na,J}$	
				K$^+$	Ca^{2+}
PVC	no surfactant	-4.7	57.5	-1.46	-2.58
(9)	Brij 35[d]	-4.3	54.7	-0.98	-2.39
	Triton X-100[e]	-4.3	54.8	0.07	-1.39
	Tween 20[f]	-4.4	55.1	-0.99	-1.17
	Tween 80[g]	-4.5	56.3	-1.16	-1.26
PVC/PU	no surfactant	-4.0	44.8	-1.38	-1.93
(10)	Brij 35	-4.1	49.5	-1.13	-2.14
	Triton X-100	-4.2	50.3	-0.08	-1.52
	Tween 20	-4.2	51.0	-1.16	-1.39
	Tween 80	-4.2	51.8	-1.26	-1.56
PU	no surfactant	-3.8	35.6	-1.28	-1.34
(11)	Brij 35	-3.7	29.8	-0.99	-1.41
	Triton X-100	-3.8	30.2	-0.04	-1.08
	Tween 20	-3.7	30.9	-1.06	-0.99
	Tween 80	-3.8	33.9	-1.08	-1.18
SR	no surfactant	-4.6	53.0	-0.86	-0.52
(12)	Brij 35	-4.6	54.4	-0.65	-0.46
	Triton X-100	-4.4	52.5	0.06	-0.97
	Tween 20	-4.5	55.1	-1.29	-0.91
	Tween 80	-4.4	51.7	-1.41	-0.84

[a]log[Na$^-$]. [b]Response slopes in mV/decade with respect to [Na$^-$] (range: 10^{-4}-10^{-1} M). [c]Potentiometric selectivity coefficient were determined according to the separate solution-matched potential method (IUPAC SSM II method). [d]0.05 wt% Brij 35, [e]0.05 wt% Triton X-100, [f]0.05 wt% Tween 20, [g]0.05 wt% Tween 80.

Table 6. Potentiometric properties of the sodium VI-based sodium-selective membranes in the absence and presence of nonionic surfactants

Matrix (No.)	condition	detection limit[a]	slope[b]	$\log K^{pot\ c}_{Na,J}$	
				K$^+$	Ca^{2+}
PVC	no surfactant	-5.2	55.6	-1.99	-4.30
(13)	Brij 35[d]	-4.8	55.6	-1.13	-4.35
	Triton X-100[e]	-4.6	53.6	0	-3.41
	Tween 20[f]	-4.7	55.1	-1.30	-4.35
	Tween 80[g]	-4.9	54.5	-1.40	-4.37
PVC/PU	no surfactant	-4.8	52.9	-1.94	-4.18
(14)	Brij 35	-4.4	52.9	-1.18	-4.26
	Triton X-100	-4.1	49.1	0	-3.06
	Tween 20	-4.4	52.5	-1.30	-4.00
	Tween 80	-4.5	52.5	-1.38	-4.06
PU	no surfactant	-4.7	50.8	-1.92	-3.87
(15)	Brij 35	-4.3	50.5	-1.21	-4.24
	Triton X-100	-4.0	46.8	-0.02	-2.91
	Tween 20	-4.3	51.1	-1.29	-3.79
	Tween 80	-4.3	50.1	-1.36	-3.76
SR	no surfactant	-4.6	53.5	0.34	-1.60
(16)	Brij 35	-4.5	54.4	0.63	-1.61
	Triton X-100	-4.4	54.9	0.57	-2.46
	Tween 20	-4.6	57.2	-1.01	-2.65
	Tween 80	-4.4	54.6	-0.95	-1.92

[a]log[Na$^-$]. [b]Response slopes in mV/decade with respect to [Na$^+$] (range: 10^{-4}-10^{-1} M). [c]Potentiometric selectivity coefficient were determined according to the separate solution-matched potential method (IUPAC SSM II method). [d]0.05 wt% Brij 35, [e]0.05 wt% Triton X-100, [f]0.05 wt% Tween 20. [g]0.05 wt% Tween 80.

four neutral carriers. The potential shifts resulting from non-ionic surfactants are clearly seen below 10^{-4} M sodium concentrations. and depend greatly on the neutral carrier doped in PVC membrane: the extent of shift was largest with MME. followed by calix[4]arene. ETH 2120. and Sodium VI. Tables 4. 5 and 6 summarize the experimental results for each ionophore.

As observed with the MME-based membranes. the presence of surfactants in sample solutions generally deteriorated the detection limits and reduced response slopes of all membrane systems. However. the extent of deterioration was largely dependent on the type of polymer matrix. neutral carrier and the kinds of nonionic surfactants. The changes in potentiometric properties in the presence and absence of nonionic surfactants were generally larger with the PVC-based membranes. indicating higher affinity to polyether type surfactants. Especially. the pronounced decrease in sodium selectivity for the PVC-based membranes suggests that the nonionic surfactants partitioned into the membrane phase effectively compete with the sodium-selective neutral carrier to bind interfering ions. On the other hand. such changes were much less with the SR-based membranes. For example. the SR-based membranes containing calix[4]arene. which provide comparable electroanalytical performance to that of the same neutral carrier containing PVC-based one in the absence of surfactants. exhibited slightly reduced sodium selectivity in the presence of Brij and Tween nonionic surfactants.

Table 7. Potentiometric properties of the valinomycin-based potassium-selective membranes in the absence and presence of nonionic surfactants

Matrix (No.)	condition	detection limit[a]	slope[b]	log $K_{K,J}^{pot}$ [c]	
				Na⁻	Ca²⁺
PVC (17)	no surfactant	-5.9	58.2	-4.37	-4.88
	Brij 35[d]	-6.0	58.0	-4.28	-4.89
	Triton X-100[e]	-5.9	58.3	-3.66	-4.65
	Tween 20[f]	-6.2	58.4	-4.22	-4.74
	Tween 80[g]	-5.8	57.9	-4.33	-4.91
PVC/PU (18)	no surfactant	-5.9	58.2	-4.28	-4.87
	Brij 35	-6.1	57.5	-4.16	-4.63
	Triton X-100	-5.7	57.6	-3.36	-4.57
	Tween 20	-6.1	57.5	-4.16	-4.63
	Tween 80	-6.0	58.1	-4.24	-4.80
PU (19)	no surfactant	-5.4	55.5	-3.64	-4.81
	Brij 35	-5.5	52.1	-3.84	-4.80
	Triton X-100	-5.2	52.8	-3.03	-3.79
	Tween 20	-5.7	57.0	-3.77	-4.22
	Tween 80	-5.8	56.8	-4.06	-4.67
SR (20)	no surfactant	-5.8	57.7	-4.31	-4.60
	Brij 35	-6.0	58.2	-4.25	-4.86
	Triton X-100	-6.0	57.9	-3.87	-4.89
	Tween 20	-5.6	57.2	-4.31	-4.93
	Tween 80	-5.8	58.1	-4.20	-4.80

[a]log[K⁻]. [b]Response slopes in mV/decade with respect to [K⁻] (range: 10⁻⁵-10⁻¹ M). [c]Potentiometric selectivity coefficient were determined according to the separate solution-matched potential method (IUPAC SSM II method). [d]0.05 wt% Brij 35. [e]0.05 wt% Triton X-100. [f]0.05 wt% Tween 20. [g]0.05 wt% Tween 80.

It is noteworthy that the potentiometric properties of sodium-selective membranes vary largely with the combination of polymer matrix and neutral carrier. For example, while the Sodium VI is contained in PVC matrix becomes sodium selective (over potassium and calcium), the same carrier in SR matrix exhibits reversed trends. The presence of Tween 20 and 80 surfactants turned SR matrix/Sodium VI membrane system into a sodium-selective one. The SR-based membranes exhibited enhanced sodium selectivity or less decrease in their sodium selectivity in the presence of Tween surfactants. In general, the effect of Tween surfactants was less significant than Triton X-100 for all sodium-selective membrane systems. Browsing the Table 3 through Table 6, one may find that the addition of a nonionic surfactant into sample or calibration solutions effect analytically significant changes in the potentiometric properties of sodium-selective membrane systems regardless of their matrix or neutral carrier.[9] These results thus suggest that the sodium-selective electrodes should be used with much care on the composition of sample or calibration solutions. If the use of a surfactant is unavoidable, Tween 20 or 80 may be recommended with SR matrix/calix[4]arene membrane system.

Effect on the Potassium Ion-Selective Electrodes. The surfactant effect for the membranes doped with valinomycin, the most widely used potassium-selective neutral carrier owing to its high potassium selectivity over other cations,

was examined. Valinomycin-based membranes exhibited much less change in their potentiometric properties in the presence of nonionic surfactants compared to sodium-selective membranes; in general, the changes in the detection limits and response slopes were not significant. However, the potassium selectivity over sodium of all membranes was significantly lowered by about 4.5 fold in the presence of Triton X-100. As was observed with sodium-selective membranes, it is presumed that Triton X-100 extracted into the membrane unselectively bind alkali metal ions and reduce the selectivity for primary ion.

PU-containing membranes are often used to achieve improved biocompatibility for biomedical application even though they tend to result in higher detection limits with reduced response slopes. However, the effect of nonionic surfactants has not been reported yet. Figure 3 shows the potentiometric response curves of the PU/valinomycin-membrane based ISE; notable EMF shifts are observed below 10⁻³ M in the presence of various surfactants. As summarized in Table 7, the presence of non-ionic surfactant, especially Triton X-100, lowered the potassium selectivity over sodium to -3.0 for PU and -3.4 for PVC/PU membranes, which is below the clinically required value ($\log K_{K,Na^+}^{POT}$ = -3.6).[13] Hence, the potential shift and loss of selectivity for PU-containing membranes in the presence of certain surfactant may result in significant error in the measurement of blood samples. Our results indicate that the potassium-selective membranes based on PU/PVC in combination with Tween 20 or Tween 80 surfactants seem to be the right choice for biomedical applications.

Effect on the Calcium Ion-Selective Electrodes. Of the known calcium ionophores, the most widely used ETH 1001 (Fluka calcium ionophore I) was investigated with various matrix systems in the absence and presence of the nonionic surfactants. The potentiometric responses determined for membranes doped with ETH 1001 are summarized in Table 8; the presence of surfactants in the sample solution did not affect much on their EMF responses to primary ion regardless of the matrices used. However, the ETH 1001-based membrane systems exhibited marked change in their selectivity over interfering ion depending on the polymer matrix and the kind of surfactants used. For most ISEs based on solvent polymeric membranes, PVC provides the best potentiometric performances. However, the ETH 1001-based membranes fabricated with other three matrices exhibited enhanced calcium selectivity over interfering ions than PVC membrane. Especially, the calcium selectivity of SR-based membrane was remarkably improved compared to that of PVC-based ones. One may see from Figure 4 that the SR-based calcium-selective membrane shows no significant potential shift in the presence of nonionic surfactants.

As observed for the sodium- and potassium-selective membranes, the ETH 1001-based membranes also exhibited largest change in their calcium selectivity over sodium and potassium in the presence of Triton X-100 than other surfactants. It is interesting to note that the calcium selectivity over potassium was affected more than that over

Table 8. Potentiometric properties of the ETH 1001-based calcium-selective membranes in the absence and presence of nonionic surfactants

Matrix (No.)	condition	detection limit[a]	slope[b]	$\log K_{Ca,J}^{pot\ c}$	
				Na^{+}	K^{+}
PVC	no surfactant	-6.7	28.7	-3.48	-3.95
(21)	Brij 35[d]	-6.5	28.6	-3.25	-2.28
	Triton X-100[e]	-5.6	28.4	-1.94	0
	Tween 20[f]	-6.5	28.9	-3.08	-1.73
	Tween 80[g]	-6.3	29.1	-3.20	-2.34
PVC/PU	no surfactant	-6.6	28.3	-4.20	-4.59
(22)	Brij 35	-6.4	28.2	-4.27	-3.77
	Triton X-100	-5.6	27.9	-3.14	-1.64
	Tween 20	-6.4	28.8	-4.11	-3.17
	Tween 80	-6.4	28.8	-4.19	-3.61
PU	no surfactant	-6.6	28.2	-4.44	-4.85
(23)	Brij 35	-6.4	28.3	-4.55	-4.24
	Triton X-100	-5.7	27.6	-3.52	-2.24
	Tween 20	-6.4	28.8	-4.43	-3.61
	Tween 80	-6.4	28.9	-4.50	-4.07
SR	no surfactant	-6.7	28.6	-4.96	-5.50
(24)	Brij 35	-6.5	25.1	-4.70	-3.52
	Triton X-100	-5.7	13.1	-5.08	-3.32
	Tween 20	-6.5	28.2	-4.60	-5.30
	Tween 80	-6.0	27.8	-5.00	-6.00

[a]log[Ca²⁻], [b]Response slopes in mV/decade with respect to [Ca²⁺] (range: 10^{-5}-10^{-1} M). [c]Potentiometric selectivity coefficient were determined according to the separate solution-matched potential method (IUPAC SSM II method). [d]0.05 wt% Brij 35, [e]0.05 wt% Triton X-100, [f]0.05 wt% Tween 20, [g]0.05 wt% Tween 80.

sodium by the presence of Triton X-100 and Brij 35. On the other hand, Tween 20 and 80 did not alter or even improved the calcium selectivity of SR-based membranes compared to that observed with no surfactant. Since SR-based membranes are known to provide improved biocompatibility over PVC-based ones, it is concluded that the SR-based membranes containing ETH 1001 in combination with Tween surfactants may provide satisfactory analytical results for biomedical applications.

Conclusion

The use of surfactants in biomedical applications is often unavoidable to wash out the adsorbed proteins, cells, and other particulates from the surface of ISE membranes. However, solvent polymeric membrane-based ISEs exhibit reduced response slopes, deteriorated detection limits (about 10-fold), and lower or even reversed primary ion selectivity over interfering ions. Such effects could be minimized by selecting proper membrane compositions (polymer matrix, plasticizer, lipophilic additives and ionophore) and matching nonionic surfactants. We examined the effect of nonionic surfactants on the potentiometric properties of sodium-, potassium- and calcium-selective membranes which are prepared with widely used ionophores and four kinds of polymer matrices (PVC, PU, PVC/PU, and SR). It was
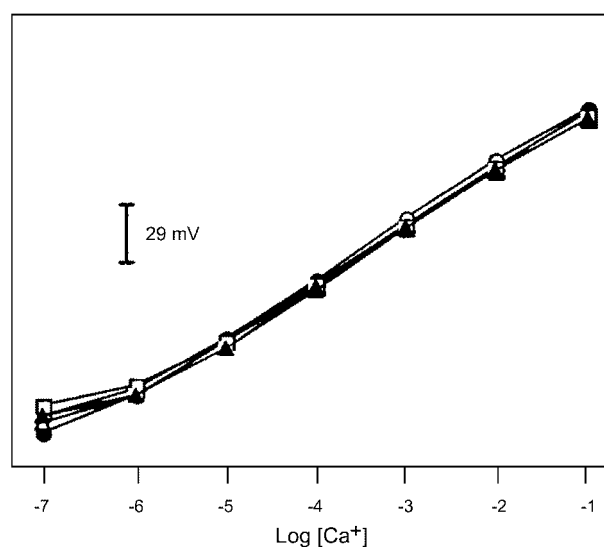

Figure 4. Potentiometric response curves of the calcium-selective electrode based on silicone rubber (SR) and (-)-R,R-N,N'-(bis(11-ethoxycarbonyl)undecyl)-N,N'-4,5-tetramethyl-3,6-dioxaoctanediamide (ETH 1001) in the absence of surfactant (○) and presence of 0.05 wt% Brij 35 (●), Triton X-100 (□), Tween 20 (△) and Tween 80 (▲).

found that the PVC-based membranes, which provide the best performance among all other matrix-based membranes in the absence of nonionic surfactants, exhibited larger change in their potentiometric properties when nonionic surfactants are added to the sample solution. Hence, care must be taken in the use of PVC-based membranes with the calibration and/or sample solutions containing nonionic surfactants. On the other hand, the sodium-selective SR-based membrane with calix[4]arene, potassium-selective PVC/PU- or SR-based membrane with valinomycin, and the calcium-selective SR-based membrane with ETH 1001 provide almost identical analytical performance in the presence and absence of Tween 20 or Tween 80 surfactants. Furthermore, the SR-based and PU-containing membranes are known to exhibit improved biocompatibility for physiological fluid. The origin of nonionic surfactants effect was also investigated by interpreting the experimental results obtained with various matrices and ionophores. The results suggest that the nonionic surfactant extracted into the membrane phase unselectively form complexes with the primary and interfering ions, resulting in increased background potential and lower binding ability for the ionophore. Such effects should result in deteriorated detection limits, reduced response slopes and lower selectivity for the primary ions.

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