

Titrimetric determination of anionic surfactant content in anionic/nonionic surfactant mixture solution by anionic surfactant selective electrode

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A new polyvinyl chloride (PVC) membrane electrode for determining the concentration of sodium dodecylsulfate (SDS) based on a neutral ion pair complex of dodecyltrimethylammonium-dodecylsulfate ($\text{DTA}^+ \text{DS}^-$) as ionophore is described in this paper. The construction and characteristic performance of the PVC membrane electrode displays a Nernstian slope of -56.9 ± 0.3 mV/decade in the concentration range of 2.0×10^{-6} to 3.2×10^{-3} mol L⁻¹ and a detection limit of 1.6×10^{-6} mol L⁻¹. The lifetime of the electrode is more than 3 months without showing significant change in the values of slope or linear concentration range. The electrode has wide pH range of application and short response time. The electrode shows selective response to DS^- and poor response to common anions except DBS^- . The electrode was used as an end point indicator electrode for the determination of SDS content in sodium dodecylsulfate/nonylphenol ethoxylates (SDS/NP-10) mixture solution by potentiometric titration using Hyamine standard solution as titrant. The maximum mol ratio ($n_{(\text{NP}-10)} : n_{(\text{SDS})}$) when SDS cannot be determined in SDS/NP-10 mixture solution can be obtained.

Key Words: Anionic surfactant selective electrode, anionic surfactant, mixture solution, potentiometric titration

Introduction

Anionic surfactants are essential for our daily life, and they are widely used in washing agents, household detergents, and personal care products. Due to their extensive use, it is quite usual to find those anions in

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the environment. Therefore, it is important to determine the concentration of these surfactants accurately in various samples. Traditional analysis methods of anionic surfactant concentration require tedious procedures or the use of large amounts of undesired solvents.¹⁻⁴ An alternative to these methods is the use of electrodes (such as ion-selective electrodes⁵⁻¹⁰ or ion-selective field-effect transistors).¹¹⁻¹⁵ Potentiometric methods using ion-selective electrodes provide many advantages such as low cost, sensitive, reliability, reproducibility, and non-destructive analysis.¹⁶⁻¹⁸ Moreover, ion-selective electrodes are simple analytical devices for determining monomer concentrations of surfactants in solution by direct potentiometry according to a Nernstian equation^{19,20} or potentiometric titration. Surfactant titrations are based on an antagonist reaction, where an ionic surfactant reacts with an oppositely charged ion, forming a water insoluble salt (ion pair),²¹⁻²⁴ when the oppositely charged ion surfactants react with each other at equal mol, the potential of the electrode has great change, and the end-point can be detected by the electrode.

The use of surfactant selective electrodes for the potentiometric determination of anionic surfactants concentration has been described in several papers. The surfactant selective electrode based on single walled carbon nanotubes constructed by Najafi et al.²⁵ was used to determine the concentration of CTA⁺ and DS⁻. Juan Soto and co-workers^{1,26} constructed an ion-selective electrode for anionic surfactants using a new aza-oxa-cycloalkane and cyclam derivative as active ionophore in PVC membrane.

The present work investigates the preparation of stable, long life, and fast response of an anionic surfactant selective electrode. The PVC membrane electrode is based on DTA⁺DS⁻ ion pair as the ionophore and DOP as plasticizer. The accurate concentration of anionic surfactants can be determined by direct potentiometry, and also the content of anionic surfactants in anionic/nonionic surfactant mixture solution can be detected by potentiometric titration.

Experimental

Sodium dodecylsulfate (SDS), dodecyl trimethyl ammonium bromide (DTAB), Hyamine, sodium dodecylbenzenesulfonate (SDBS), and high molecular weight PVC were from Aldrich (analytical grade). Bis-(2-ethylhexyl) phthalate (DOP) and tetrahydrofuran (THF) were both from Tianjin Kermel Chemical Reagent Company. All other reagents used for the preparation of the electrode were analytical grade. Distilled water was used for the preparation of the solutions and for the cleaning of all glassware and apparatus in the experiments.

The potentiometric measurements were performed with a pH^s 3C pH/mV meter, and a saturated calomel electrode (SCE) was used as external reference electrode. The pH^s 3C pH/mV meter and saturated calomel electrode were purchased from Shanghai Precision and Scientific Instrument Co., Ltd. The indicator electrode used for potentiometric titrations was a self-made anionic surfactant selective electrode. Potentiometric titrations were conducted with the help of an automatic burette and a titriprocessor (Beijing Xianquweifeng Technology Development Company) using a 25.0 ± 0.1 °C water-thermostated vessel and an automatic burette.

The surfactant ion-selective electrode was made according to the classical method described as the literature²⁷ and the preparation can be formulated as follows.

The DTA⁺DS⁻ ion pair was prepared by pouring together equimolar amounts of SDS and DTAB in hot aqueous solution. The ion pair DTA⁺DS⁻ was formed as a white precipitate, which was filtered off, washed with distilled water, and recrystallized twice from hot acetone.

The membranes with PVC:DOP 2:3 contained 1.0×10^{-3} mol DTA⁺DS⁻ ion pair/kg (PVC+DOP). PVC, DOP, and DTA⁺DS⁻ ion pair were dissolved in tetrahydrofuran, and then poured into a flat-bottomed glass dish. Tetrahydrofuran evaporated from the solution at room temperature for 48 h, and then the required membrane was obtained.

A disk of 0.5 cm in radius was cut from the obtained membrane and attached to the end of a PVC tube using the solution of PVC dissolved in THF as adhesive. The Ag/AgCl electrode was used as inner reference electrode. As inner solution 1.0×10^{-3} mol L⁻¹ SDS and 1.0×10^{-3} mol L⁻¹ KCl mixture solution was used. Before the first use the electrode was preconditioned in 1.0×10^{-3} mol L⁻¹ SDS solution for 24 h.

The external reference electrode was a saturated calomel electrode (SCE), and the self-made electrode was used for all emf measurements. Potentiometric measurements were carried out by the following cell assembly: SCE | Saturated KCl solution | sample solution | PVC membrane | inner solution | Ag/AgCl. All potential measurements were carried out on a pH^s 3C pH/mV meter.

The response to SDS was measured in the concentration range of 1.7×10^{-7} to 1.9×10^{-2} mol L⁻¹ SDS solutions, and also 1.0×10^{-6} to 1.0×10^{-3} mol L⁻¹ NP-10 solutions were measured using the electrode. The indicator electrode was stored in air without drawing out the inner solution during the life time studies. Potentiometric selectivity coefficients were determined according to the fixed interference method using 2.5×10^{-2} mol L⁻¹ solution of interfering ion. Calibration curves were constructed by plotting the potential (*E*) versus the logarithm of the SDS concentration. The volume of tested solution used for titration was 25.0 mL. The titrant dosage rate was 0.1 mL s⁻¹. The titrants were 4.12×10^{-3} and 4.88×10^{-2} mol L⁻¹ Hyamine standard solutions. They were used for the titrations of 5.0×10^{-4} and 5.0×10^{-3} mol L⁻¹ SDS mixture solution, respectively. All the measurements and titration were performed at 25.0 ± 0.1 °C.

Results and discussion

Response behavior of the electrode

The potentiometric analysis method with an anionic surfactant selective electrode was developed for the determination of anionic surfactants. Surfactant concentration and potential comply with the following Nernstian equation:

$$E = E^\circ + 2.303 \frac{RT}{zF} \log a_{DS^-} \quad (1)$$

where *E* stands for the equilibrium electrode potential, *E*[°] is the standard electrode formal potential, *R* is the gas constant, *T* is the temperature, *z* is the ion charge number, *F* is the Faraday's constant, and *a*_{DS⁻} is the activity of SDS solution. Therefore, the surfactant concentration can be obtained from the potentiometry measured using a surfactant ion-selective electrode.

The response characteristics of the anionic surfactant electrode in SDS and NP-10 solutions are shown in Figure 1. It can be seen that the electrode had good Nernstian response to different concentration of SDS. The potential response to various concentration of NP-10, however, was constant, which did not comply with the Nernstian equation. The results indicated that the electrode had good selectivity to SDS.

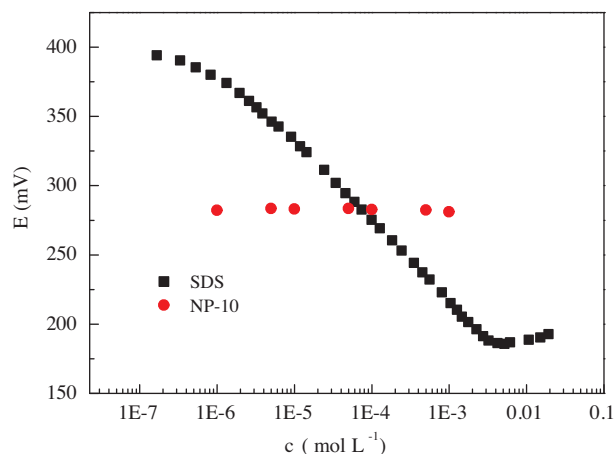


Figure 1. Potential response of anionic surfactant selective electrode to SDS solutions (■) and NP-10 solutions (●).

Statistical evaluation of the electrode characteristics for SDS is given in Table 1.

Table 1. Response parameters of anionic surfactant selective electrode for SDS solution.

Parameters	Values
Slope (mV/decade)	-56.9 ± 0.3
Correlation coefficient (r)	0.9996
Detection limit (mol L ⁻¹)	1.6×10^{-6}
Linear concentration range (mol L ⁻¹)	$2.0 \times 10^{-6} \sim 3.2 \times 10^{-3}$

The slope value and correlation coefficients were calculated from the linear region of the calibration graph of the measurements using linear regression analysis. Detection limit was defined as the concentration of SDS corresponding to the intersection of the extrapolated linear segments of the calibration graph,²⁸ which was 1.6×10^{-6} mol L⁻¹. The electrode showed linear Nernstian response with the slope of -56.9 ± 0.3 mV/decade in the concentration range of 2.0×10^{-6} to 3.2×10^{-3} mol L⁻¹ for SDS.

Response time

The response time of the electrode was measured after successive immersion of the electrode in a series of different concentration SDS solutions from 1.0×10^{-6} to 1.0×10^{-3} mol L⁻¹. The response time of the electrode was evaluated by measuring the time required to achieve a steady-state potential.^{29,30}

As shown in Figure 2, a response time about 30 s was found as the time required for the electrode to reach a potential within ± 1 mV of the final equilibrium. The standard deviation of the response time calculated from 4 measurements was ± 3 s, and so the response time of the electrode was 30 ± 3 s.

Effect of pH

The influence of pH on the potential response of the electrode was studied at a fixed concentration of SDS of 1×10^{-4} mol L⁻¹ over the pH range of 2.0-12.3.

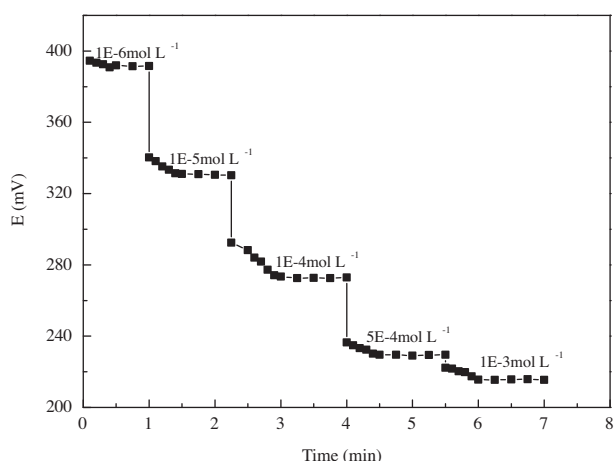


Figure 2. Response time of anionic surfactant selective electrode for step changes in different concentration SDS solutions.

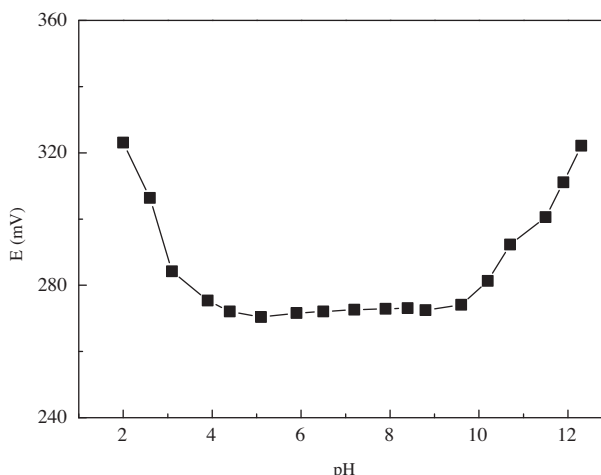


Figure 3. Effect of pH on the potentials of anionic surfactant selective electrode in $1 \times 10^{-4} \text{ mol L}^{-1}$ SDS solution.

At low pH, DS^- combined with H^+ and then HDS formed. The concentration of DS^- was decreased in the solution, which is probably related to the increasing of HDS concentration. When the pH values were higher than 9.6, the potential of the electrode was also affected. Potential increased most likely due to the fact that the membrane had a response to the OH^- , because of OH^- ions competing with DS^- ions in such a medium. Therefore, potentials remained constant between pH 4.4-9.6 as illustrated in Figure 3, and pH 7 was chosen as optimum pH for the studies.¹

Life time of the electrode

The electrode characteristics obtained at various time intervals are illustrated in Table 2 and Figure 4. The electrode exhibited good reproducibility in slope, linear concentration range, and detection limit for 14 weeks,

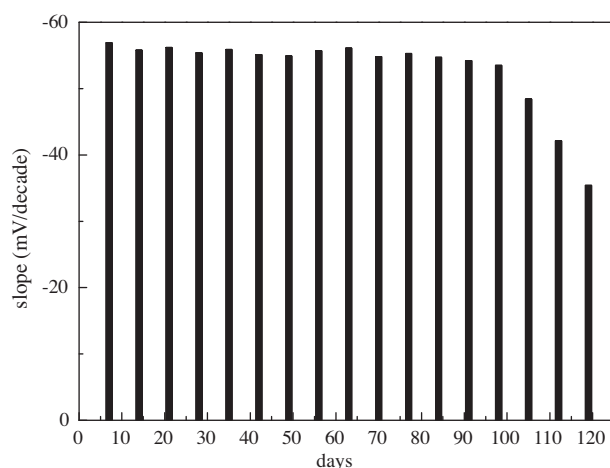


Figure 4. Plot of the slope of anionic surfactant selective electrode in the presence of DS^- vs. time (days).

but drifts of the slope and detection limit were observed after 15 weeks. The life time of the electrode was more than 3 months.¹

Table 2. The life time study of anionic surfactant selective electrode.

Period (weeks)	Slope (mV/decade)	Linear range (mol L ⁻¹)	Detection limit (mol L ⁻¹)
1	-56.9	2.0×10^{-6} to 3.2×10^{-3}	1.6×10^{-6}
2	-55.8	1.9×10^{-6} to 3.1×10^{-3}	1.4×10^{-6}
3	-56.2	2.1×10^{-6} to 3.0×10^{-3}	1.5×10^{-6}
4	-55.4	2.2×10^{-6} to 3.3×10^{-3}	1.7×10^{-6}
5	-55.9	1.9×10^{-6} to 3.4×10^{-3}	1.6×10^{-6}
6	-55.1	2.1×10^{-6} to 3.3×10^{-3}	1.5×10^{-6}
7	-54.9	2.2×10^{-6} to 3.5×10^{-3}	1.4×10^{-6}
8	-55.7	2.2×10^{-6} to 3.3×10^{-3}	1.6×10^{-6}
9	-56.1	2.0×10^{-6} to 3.4×10^{-3}	1.8×10^{-6}
10	-54.8	1.9×10^{-6} to 3.2×10^{-3}	1.5×10^{-6}
11	-55.3	2.2×10^{-6} to 3.4×10^{-3}	1.7×10^{-6}
12	-54.7	2.1×10^{-6} to 3.2×10^{-3}	1.8×10^{-6}
13	-54.2	2.4×10^{-6} to 3.4×10^{-3}	1.6×10^{-6}
14	-53.5	2.9×10^{-6} to 3.5×10^{-3}	2.1×10^{-6}
15	-48.5	4.1×10^{-6} to 3.2×10^{-3}	2.9×10^{-6}
16	-42.1	6.6×10^{-6} to 3.5×10^{-3}	4.8×10^{-6}
17	-35.4	9.4×10^{-6} to 4.0×10^{-3}	8.1×10^{-6}

Determination of potentiometric selectivity coefficients

We carried out several studies with the electrode for response to SDS in the presence of interfering ions. As can be seen in Figure 5, the electrode displayed a remarkable selective response to SDS, and a very poor change in the potential in the presence of the anions, Cl⁻, Br⁻, SO₄²⁻, PO₄³⁻, CH₃COO⁻, C₂O₄²⁻, and C₆H₅O₇³⁻, except DBS⁻.

In order to quantify the selective behavior of the electrode towards SDS, we carried out studies to determine potentiometric selectivity coefficients. The potentiometric selectivity coefficients (k_{DS^-,X^-}^{pot}) of the electrode were calculated by means of fixed interference method considering SDS as the principal anion and using a concentration of 2.5×10^{-2} mol L⁻¹ for interfering anions. k_{DS^-,X^-}^{pot} was calculated with Eq. (2):³¹

$$K_{ij}^{pot} = \frac{a_{DS^-}}{(a_{X^-})^{z_{DS^-}/z_{X^-}}} \quad (2)$$

where a_{DS^-} is the activity of DS⁻, a_{X^-} is the activity of the corresponding interfering ion, and z_{DS^-} and z_{X^-} are the corresponding charge of the primary ion and the interfering ion, respectively. The potentiometric selectivity coefficients are listed in Table 3. The selectivity sequence for the electrode was DBS⁻ > CH₃COO⁻ >

$\text{Cl}^- > \text{Br}^- > \text{C}_6\text{H}_5\text{O}_7^{3-} > \text{C}_2\text{O}_4^{2-} > \text{SO}_4^{2-} > \text{PO}_4^{3-}$. The logarithm of the potentiometric selectivity coefficients lower than -3.0 except DBS^- indicated that most of the anions would not disturb the determination of SDS in real samples.

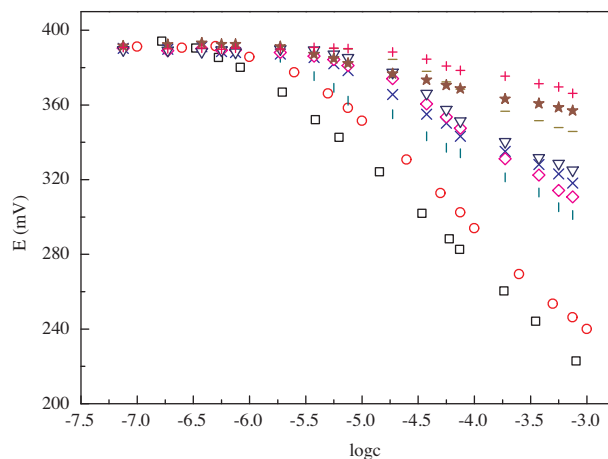


Figure 5. Response of anionic surfactant selective electrode in the presence of certain anions: (□) SDS; (○) SDBS; (×) Cl^- ; (|) Br^- ; (◇) SO_4^{2-} ; (-) PO_4^{3-} ; (▽) CH_3COO^- ; (★) $\text{C}_2\text{O}_4^{2-}$; (+) $\text{C}_6\text{H}_5\text{O}_7^{3-}$.

Table 3. Potentiometric selective coefficients for anionic surfactant selective electrode.

Interfering ion	$k_{DS^-,X^-}^{pot}(\log)$	Interfering ion	$k_{DS^-,X^-}^{pot}(\log)$
Cl^-	-3.89	CH_3COO^-	-3.55
Br^-	-4.24	$\text{C}_2\text{O}_4^{2-}$	-4.72
SO_4^{2-}	-4.91	$(\text{C}_6\text{H}_5\text{O}_7^{3-})^a$	-4.47
PO_4^{3-}	-5.06	DBS^-	4.21

^acitrate

Analytical application

Our investigations showed that the electrode cannot only be used for direct determination of SDS, but also can be used as an end-point indicator electrode in titration of SDS with Hyamine standard solution. As an example, it was applied in the titration of SDS in SDS/NP-10 mixture solutions with Hyamine. The content of SDS in the mixture solutions can be accurately determined by the electrode, and also the maximum mol ratio ($n_{(NP-10)} : n_{(SDS)}$) when SDS cannot be determined in SDS/NP-10 mixture solution can be obtained.

In order to determine the concentration of SDS and obtain the result of maximum mol ratio ($n_{(NP-10)} : n_{(SDS)}$) when SDS cannot be determined in SDS/NP-10 mixture solutions. We fabricated 2 teams of SDS/NP-10 mixture solutions (team 1 (samples 1-8) and team 2 (samples 9-16), the concentration of SDS was fixed as $5.0 \times 10^{-4} \text{ mol L}^{-1}$ and $5.0 \times 10^{-3} \text{ mol L}^{-1}$ respectively, and then the concentration of NP-10 in the mixture solution increased in turn).

The electrode was used for the determination of SDS content in various mol ratio ($n_{(NP-10)} : n_{(SDS)}$) SDS/NP-10 mixture solutions by potentiometric titration in conjunction with SCE as reference electrode. A series of typical sigmoid shape titration curves obtained from the titration of SDS are shown in Figures 6 and 7.

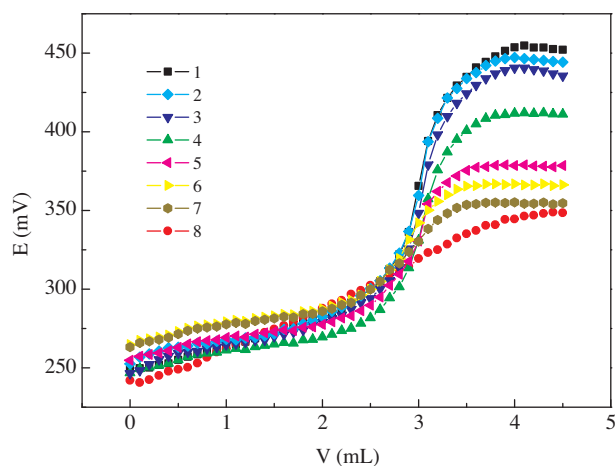


Figure 6. Titration curves of SDS with Hyamine in SDS/NP-10 mixture solutions. The concentration of SDS was fixed as $5.0 \times 10^{-4} \text{ mol L}^{-1}$ in the mixture solutions. The mole ratio ($n_{(NP-10)} : n_{(SDS)}$) of curve 1-8: 0; 1:100; 1:10; 1:1; 2:1; 3:1; 4:1; 10:1.

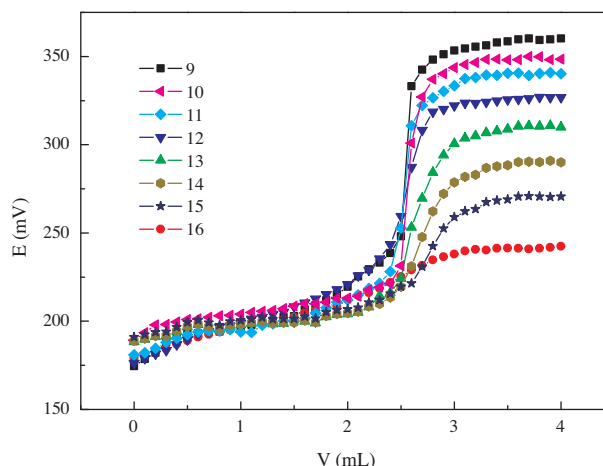


Figure 7. Titration curves of SDS with Hyamine in SDS/NP-10 mixture solutions. The concentration of SDS was fixed as $5.0 \times 10^{-3} \text{ mol L}^{-1}$ in the mixture solutions. The mole ratio ($n_{(NP-10)} : n_{(SDS)}$) of curve 9-16: 0; 1:100; 1:10; 1:1; 2:1; 3:1; 4:1; 10:1.

Each titration volume estimated at the inflection point of the titration curve is shown in Tables 4 and 5. From Figures 6 and 7, it can be observed that with the increase in mol ratio ($n_{(NP-10)} : n_{(SDS)}$) the height of the potential jump ($\Delta E / \Delta V$) in the titration curves decreased, and the titration curves became nearly planar without potential jump at last.

From Tables 4 and 5, it can be seen that the same results for the potential jump at the end-point of titration of SDS can be detected, when the mol ratio ($n_{(NP-10)} : n_{(SDS)}$) was not more than 4:1 in both teams of SDS/NP-10 mixture solutions. The main cause was probably the increase in NP-10, which baffled the diffusion of DS^- to the electrode surface. The adsorption capacity of active DS^- reduced and double electricity layer of the electrode surface was disturbed, and so the potential jump decreased.

For the determination of SDS in commercial detergent, a 15-30 mg sample was dissolved in 2 mL of methanol and diluted to 100 mL with water and a 20 mL portion applied to the determination of SDS in samples by the electrode. The results of the potentiometric titration using the electrode were compared with those obtained using 2-phase titration. As shown in Table 6, the results recorded by the potentiometric titration are in good accordance with those given by 2-phase titration.

Table 4. Evaluation of the titration results of SDS/NP-10 mixed solution carried out with anionic surfactant selective electrode.

No	$c_{(SDS)} / \text{mol L}^{-1}$	$c_{(NP-10)} / \text{mol L}^{-1}$	$n_{(NP-10)} : n_{(SDS)}$	Equivalent point error Hyamine ^a /mL	Relative of Vep /% volume of	$\Delta E / \Delta V$
1	5.0×10^{-4}			3.01		141.6
2	5.0×10^{-4}	5.0×10^{-6}	1:100	3.03	0.66	138.5
3	5.0×10^{-4}	5.0×10^{-5}	1:10	3.04	1.00	121.5
4	5.0×10^{-4}	5.0×10^{-4}	1:1	3.05	1.32	118.5
5	5.0×10^{-4}	1.0×10^{-3}	2:1	3.03	0.66	105.4
6	5.0×10^{-4}	1.5×10^{-3}	3:1	2.99	-0.66	96.8
7	5.0×10^{-4}	2.0×10^{-3}	4:1	Without equivalent point		
8	5.0×10^{-4}	5.0×10^{-3}	10:1	Without equivalent point		

^a The concentration of Hyamine is $4.12 \times 10^{-3} \text{ mol L}^{-1}$

Table 5. Evaluation of the titration results of SDS/NP-10 mixed solution carried out with anionic surfactant selective electrode.

No	$c_{(SDS)} / \text{mol L}^{-1}$	$c_{(NP-10)} / \text{mol L}^{-1}$	$n_{(NP-10)} : n_{(SDS)}$	Equivalent point error Hyamine ^a /mL	Relative of Vep /% volume of	$\Delta E / \Delta V$
9	5.0×10^{-3}			2.55		328.1
10	5.0×10^{-3}	5.0×10^{-5}	1:100	2.56	0.39	317.6
11	5.0×10^{-3}	5.0×10^{-4}	1:10	2.53	-0.78	302.4
12	5.0×10^{-3}	5.0×10^{-3}	1:1	2.57	0.78	262.5
13	5.0×10^{-3}	1.0×10^{-2}	2:1	2.58	1.17	184.2
14	5.0×10^{-3}	1.5×10^{-2}	3:1	2.53	-1.17	86.6
15	5.0×10^{-3}	2.0×10^{-2}	4:1	Without equivalent point		
16	5.0×10^{-3}	5.0×10^{-2}	10:1	Without equivalent point		

^a The concentration of Hyamine is $4.88 \times 10^{-2} \text{ mol L}^{-1}$

Table 6. Comparison of the results obtained by potentiometric and 2-phase titration of commercial detergent.

Sample	SDS (wt%)	
	Potentiometric titration	Two-phase titration
1 ^a	16.31	16.23
2 ^a	16.34	16.26
3 ^a	16.30	16.21
RSD (%) ^b	1.68	2.05

^aNumber 1, 2, 3: washing liquid (SDS, Np-10, glycerin, NaCl, diethanolamide, additives).

^bRelative standard deviation of potentiometric titration and 2-phase titration for triplicate measurements.

Conclusions

A comparison with similar previously reported works is shown in Table 7. The response slopes to SDS of those electrodes were similar. The membrane containing new cyclic aza-oxa-cycloalkane as ionophore had the widest linear range. The membrane containing DTA⁺DS⁻ ion pair as ionophore had the widest pH usage range and the lowest detection limit. The electrode based on DTA⁺DS⁻ ion pair as ionophore in PVC membrane displayed a Nernstian slope of -56.9 ± 0.3 mV/decade in a 2.0×10^{-6} to 3.2×10^{-3} mol L⁻¹ concentration range and a limit of detection of 1.6×10^{-6} mol L⁻¹. The electrode had a short response time and wide pH range for use, and it can be used for 3 months without significant change in the value of slope and linear concentration range. The electrode was suitable for detecting the endpoint of anionic surfactant titrations. The behavior of the electrode was assessed with regard to its usefulness in routine analysis. The relative error of the endpoint volume was not more than 1.5% in SDS/NP-10 mixture solutions. Our investigations showed that the electrodes specially designed for anionic surfactant titrations did not need conditioning before use except the first time.

Table 7. Comparison with similar previously reported works.

Ionophore	Slope (mV/decade)	Linear range (mol L ⁻¹)	Detection Detection limit (mol L ⁻¹)	pH range
New cyclic aza-oxa-cycloalkane ^a	-57.7 ± 0.2	3.3×10^{-6} to 6.7×10^{-3}	2.9×10^{-6}	4.5-8.0
Cyclam derivative ^b	-60.0 ± 0.9	7.9×10^{-6} to 2.0×10^{-3}	4.0×10^{-6}	5.0-8.5
Single walled carbon nanotubes ^c	-59.5	9.0×10^{-5} to 5.0×10^{-3}	5.2×10^{-6}	Not mentioned
DTA ⁺ DS ⁻ ion pair ^d	-56.9 ± 0.3	2.0×10^{-6} to 3.2×10^{-3}	1.6×10^{-6}	4.4-9.6

^aReference [26], ^bReference [1], ^cReference [25], ^dTextual content

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