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Potentiometric Determination of Anionic Surfactants in Formulations Containing Cocoamidopropyl Betaine

Dubravka Madunić-Čačić[1], *Milan Sak-Bosnar*[*], *Ružica Matešić-Puač*[2], *Mirela Samardžić*[2]

[1] Saponia Chemical, Pharmaceutical and Foodstuff Industry, M. Gupca 2, HR-31000 Osijek, Croatia
[2] Department of Chemistry, Josip Juraj Strossmayer University of Osijek, F. Kuhača 20, HR-31000 Osijek, Croatia
[*]E-mail: msbosnar@kemija.unios.hr

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The application of surfactant sensor based on hexadecyltrioctadecylammonium-tetraphenylborate (HTA-TPB) for the potentiometric titration of anionic surfactant (SLES) in the presence of amphoteric surfactant (CAPB) is described. Standard solution of 1,3-dodecyl-2-methylimidazolium chloride (DMIC) was used as titrant (c = 2 mM). Amphoteric surfactants exhibit properties of anionic surfactants (AS) at high pH values; therefore, the exact titrimetric determination of AS in the presence of amphoteric surfactants is strongly pH dependent and should be performed at pH 4. The accuracy of this determination depends on the SLES:CAPB ratio, and its accuracy decreases with an increasing CAPB content. The significant interfering effect of CAPB on the SLES determination was evidenced when the SLES:CAPB ratio was higher than 1:1. The normal AS to amphoteric surfactant ratio for commercial products is in the range of 1:1 to 2:1, and these ratios result in recoveries of 96 - 100 %.

Keywords: ion sensitive sensor, PVC membrane, anionic surfactant, amphoteric surfactant, potentiometric titration, detergent products, personal care products

1. INTRODUCTION

Mixed systems perform better than single surfactant systems [1]. Modern liquid detergents and personal care products are multicomponent products with a number of interactions between constituents that increase product effectiveness, including the formation of self-assembling complexes that exhibit synergistic behaviors. Anionic and amphoteric surfactants are the basic surfactants used in personal care products to achieve outstanding detergency, cleansing quality, good foaming property and easy thickening in the presence of salts. In these multicomponent products, synergistic effects are achieved that lead to a dermatological improvement. The formation of large rodlike micelles has been reported in mixed solutions of sodium dodecyl sulfate (SDS) and cocoamidopropyl betaine at a relatively low total surfactant concentration [2]. Even small addition of betaine to SDS significantly increases the surface elasticity. The results could be further applied to predict the thickness and stability of foam films and the size of the rodlike micelles in the mixed solutions of SDS and betaine [3]. Betaines are widely used as foam boosters because of their ability to stabilize foams against the antifoaming action of oil droplets in commercial shampoos and hair conditioners [4,5]. Moreover, betaines are known to reduce irritation to the eyes and skin that is caused by surfactant solutions [6]. Previous studies indicate that there are strong synergistic effects in mixed solutions of SDS and C_{12}-betaine [7,8].

Alkyl sulfates and alkyl ether sulfates are commonly used anionic surfactants in liquid detergents, cosmetic cleansing preparations (shampoos, shower gels and foam baths) and pharmaceutical surfactant preparations. Commonly used methods in ionic surfactant analysis [9] are based on a so-called two-phase titration [10] that suffers from a large number of drawbacks and numerous matrix interferences.

In contrast, the potentiometric titration with ion-selective electrode (ISE) sensors overcomes most of these limitations and represents a simple, rapidly available and inexpensive method to determine surfactants.

Potentiometry with surfactant-sensitive electrodes for surfactant determination began in the 1970s [11], and a few excellent articles have reviewed the use of potentiometric sensors for surfactant analysis [12]. In the investigations described here, a self-made surfactant-sensitive liquid membrane electrode was successfully used as a potentiometric sensor for the determination of anionic surfactants in the presence of amphoteric surfactants. The membrane was composed of hexadecyltrioctadecylammonium-tetraphenylborate (HTA-TPB) as an electroactive material and *o*-nitrophenyl octyl ether (*o*-NPOE) as a plasticizer.

2. EXPERIMENTAL SECTION

2.1. Reagents and Materials

Hexadecyltrioctadecylammonium bromide (HTAB), sodium tetraphenylborate (STPB), *o*-nitrophenyl octyl ether (*o*-NPOE), high molecular-weight poly(vinyl chloride) (PVC) and tetrahydrofuran (THF) were used for the preparation of the membranes. All of the above-mentioned chemicals (Fluka, Switzerland) were of Selectophore or puriss quality.

A standard solution of 1,3-didecyl-2-methylimidazolium chloride (DMIC) (c = 2 mM) was used as a titrant. Sodium dodecyl sulfate (SDS) was used for standardizing the titrant. All of the above-mentioned chemicals were of reagent grade quality (Fluka, Switzerland).

Technical grade surfactants sodium lauryl ether sulfate (SLES, Texapon N 70, Cognis) and cocoamidopropyl betaine (CAPB, Rokamina K30, PCC Rokita) were used for the preparation of the model mixtures.

All solutions were prepared in laboratory water Grade II (BS EN ISO 3696:1995).

2.2. Instruments and Measurements

The all-purpose titrator 808 Titrando (0.1 mV resolution) combined with a Metrohm 806 Exchange unit (10 mL burette volume with an outstanding resolution of 20000 steps per cylinder volume) and controlled by the Tiamo software was used to perform potentiometric titrations. During the titrations and measurements, the solutions were magnetically stirred using a 727 Ti Stand. The abovementioned instruments were purchased from Metrohm, Switzerland.

2.3. Sensor Preparation

HTA-TPB ion pair was prepared by dissolving equimolar amounts of HTAB and STPB in dichloromethane. The solution was washed with water and dried under anhydrous sodium sulfate. After evaporation and recrystallization in a 1:1 mixture of diethylether and methanol, the isolated ion-exchanged complex was used as the sensing material (1.0 %) in the membrane preparation with *o*-NPOE as the plasticizer and high molecular-weight PVC (the plasticizer:PVC ratio was 3:2). The mixture of PVC, plasticizer and sensing material was dissolved in tetrahydrofuran and carefully poured into a glass ring that had been tightly fixed on a glass plate. After curing, small disks (7 mm i.d.) were excised from the cast film and mounted on a Philips electrode body IS-561. The detailed preparation and characterization of the sensor has been described previously [13].

A silver/silver(I) chloride reference electrode (Metrohm, Switzerland) with a reference electrolyte solution (sodium chloride, $c = 2$ M) was used as a reference.

2.4. Titration Conditions

The volume of the solution used for all titrations was 50 mL. The titrator was programmed to work in the DET (dynamic equivalent point titration) mode with a signal drift of 5 mV/min, minimum and maximum increments of 10 and 200 μL, respectively, and minimum and maximum equilibrium times of 10 and 30 s, respectively. The wait time prior to starting the titration was 90 s. All titrations were performed at room temperature with a preset *p*H.

The potentiometric titrations were performed by using the following cell assembly:

Ag/AgCl (KCl, 2 M) || test solution || liquid membrane | (NaCl, 2 M) Ag/AgCl.

3. RESULTS AND DISCUSSION

The titrimetric determination of AS was based on the reaction between AS and an oppositely charged cation of the titrant (DMI^+) accompanied by the formation of a water-insoluble salt (ion pair). The titration was carried out in one step:

$$\mathbf{DMI^+ + AS^- \rightleftharpoons DMI - AS}$$

In the presence of amphoteric surfactants such as CAPB, which can show the properties of anionic surfactants at high *p*H values and the properties of cationic surfactants at low *p*H values, AS can be titrated at *p*H values where amphoteric surfactants exist mainly as zwitterions (in the vicinity of their isoelectric points).

Therefore, the exact titrimetric determination of AS in the presence of amphoteric surfactants is strongly *p*H dependent. In the present study, the influence of the amphoteric surfactant on AS determination was examined for the *p*H range of 1 to 10.

Model solutions of two-component surfactant mixtures containing anionic and amphoteric surfactants were prepared. A model sample of a liquid hand-dishwashing detergent was also prepared, which contained a known composition of SLES as an AS and CAPB as an amphoteric surfactant. SLES and CAPB were selected because of their prevalence in commercial products later analyzed.

3.1. Titrations of Model Systems

3.1.1. A Model of a Two-Component Surfactant Mixture

A model of a two-component surfactant mixture with a defined composition of SLES as an AS and CAPB as an amphoteric surfactant (both of technical grade) was investigated.

3.1.1.1. The Influence of pH

For the study of the influence of *p*H on the accuracy of the determination of AS in the presence of an amphoteric surfactant, a two-component model solution containing known amounts of SLES (30.73 mmol/100 g) and CAPB (11.22 mmol/100 g) was prepared. Potentiometric titrations were performed with a preset *p*H in the range of 1 to 10. The titration curves and their corresponding derivatives for *p*H values between 1 and 4 are shown in Figure 1.

The results of all of the determinations in the *p*H range of 1 to 10 are shown in Table 1.

The greatest accuracy (recovery: 99.83 %) of the determination of SLES was obtained by titrating the model surfactant mixture at *p*H 4. At *p*H 4, AS reacts stoichiometrically with the cationic titrant DMIC without being influenced by the amphoteric surfactant CAPB, which is present in the model solution. The inflexion point of the titration curves obtained at *p*H 4 provided additional support for this conclusion (Figure 1).

Below *p*H 4, the recovery decreased. This observation can be explained by the increased cationic character of CAPB because of its protonation at low *p*H values. Thus, CAPB behaves as a cationic surfactant, the most pronounced cationic character of CAPB was evidenced at *p*H 1, where the recovery of the SLES determination was only 88.98 %. Slightly increased recoveries were obtained above *p*H 5, likely because of the weak anionic character of the amphoteric surfactant in neutral or basic solutions.

In conclusion, the determination of SLES in the model solution containing 30.73 mmol/100 g SLES and 11.22 mmol/100 g CAPB was most accurate at *p*H 4.

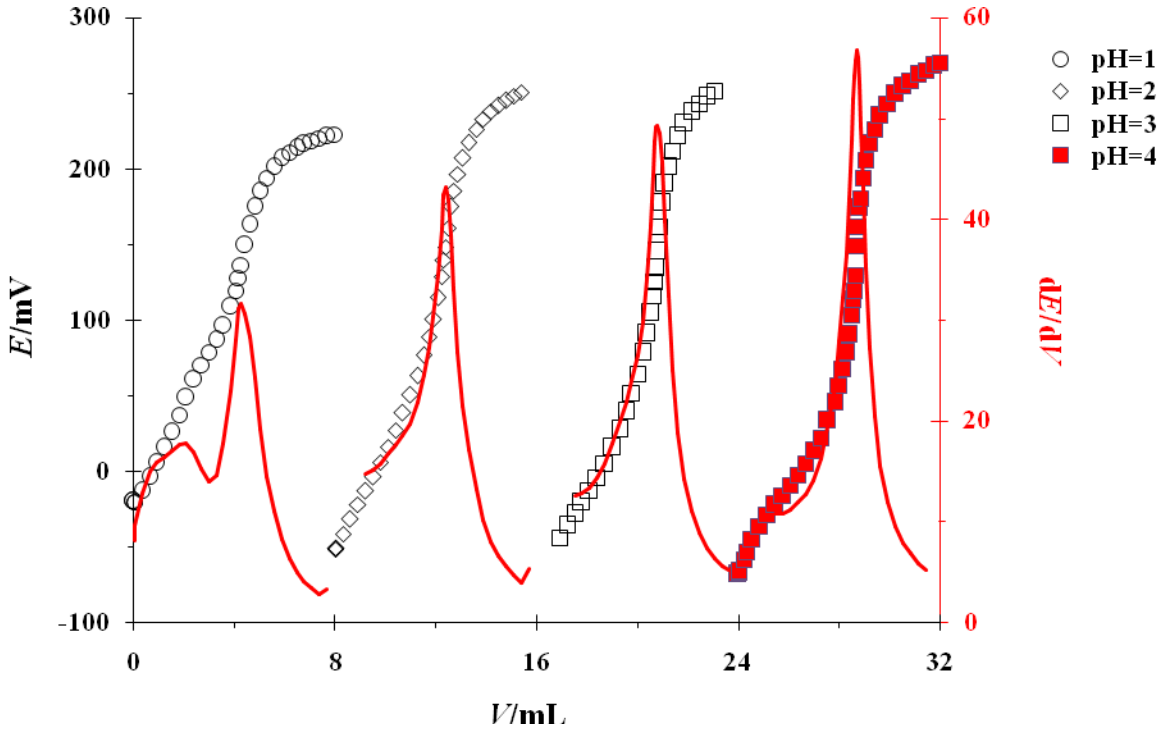

Figure 1. Influence of the *p*H on the potentiometric titration curves of a model solution containing SLES (30.37 mmol/100 g) and CAPB (11.22 mmol/100 g). The titration curves were obtained by using DMIC (c = 2 mM) as a titrant and the HTA-TPB surfactant sensor as an indicator.

Table 1. Results of the potentiometric titration of a model solution containing SLES (30.37 mmol/100 g) and CAPB (11.22 mmol/100 g) in the *p*H range of 1-10.

*p*H	SLES (mmol/100g)		Recovery (%)
	Expected	Found*	
1	30.73	27.34	88.98
2	30.73	28.28	92.03
3	30.73	30.21	98.31
4	30.73	30.68	99.83
5	30.73	30.81	100.25
6	30.73	31.09	101.19
7	30.73	31.17	101.44
8	30.73	31.22	101.61
9	30.73	31.22	101.61
10	30.73	31.17	101.44

* Average value of 3 determinations

3.1.1.2. Influence of The Ratio Between SLES And CAPB

To estimate the influence of CAPB on the determination of SLES, model solutions containing SLES and CAPB were examined for three different SLES:CAPB ratios (2:1, 1:1 and 2:3) at *p*H 4. The titration curves and their derivatives are shown in Figure 2.

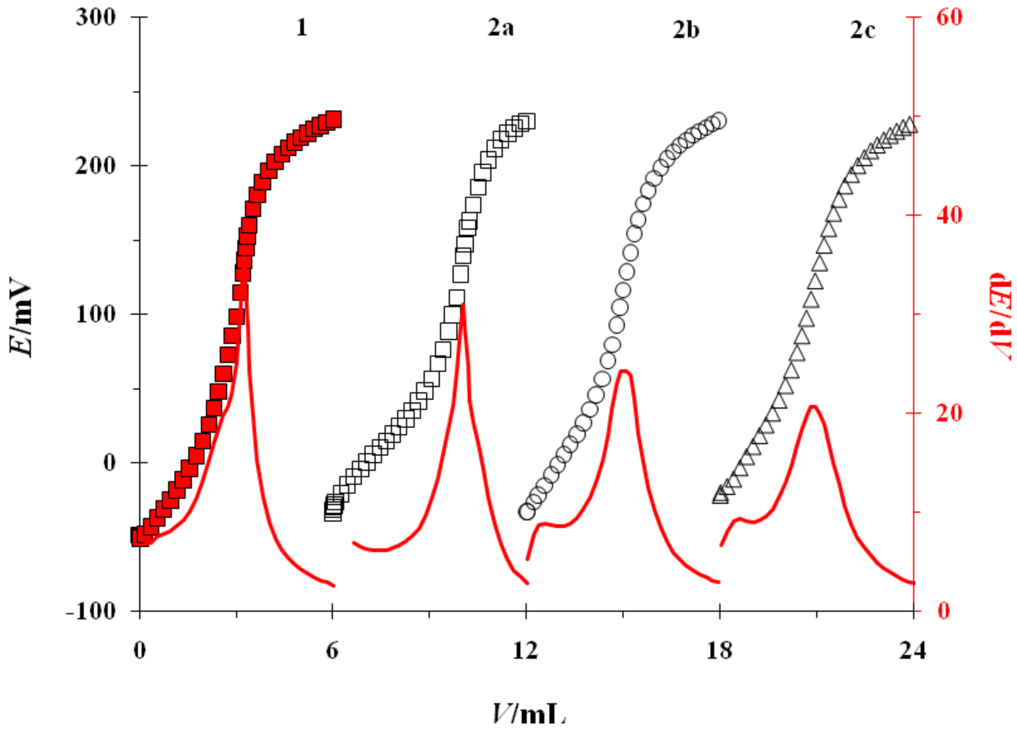

Figure 2. Potentiometric titration curves of SLES in model solutions containing three different SLES:CAPB ratios [1 – SLES; 2a – SLES:CAPB (2:1); 2b – SLES:CAPB (1:1); 2c – SLES:CAPB (2:3)]. The titration curves were obtained by using DMIC (*c* = 2 mM) as a titrant and the HTA-TPB surfactant sensor as an indicator.

The recovery obviously depends on the AS:CAPB ratio (Table 2) and decreases with an increasing content of CAPB. For the SLES:CAPB ratio of 2:1, the recovery during the determination of SLES was 99.87 %; at a SLES:CAPB ratio of 1:1, the recovery was 96.20 %. A significant interfering effect of CAPB on the SLES determination was observed when the SLES:CAPB ratio was greater than 1:1.

The influence of CAPB on the accuracy of the SLES titration at *p*H 4 (a pH at which CAPB supposedly exists in its zwitterionic state) could be explained by its neutral and surface-active character, which causes interferences that are similar to nonionic surfactants [14-16].

The normal AS to amphoteric surfactant ratio for commercial products is in the range of 1:1 to 2:1. Thus, recoveries of 96 - 100 % can be expected in the potentiometric determination of AS at *p*H 4.

Table 2. Results of the potentiometric titration of SLES in model two-component solutions containing three different SLES:CAPB ratios.

Mass ratio SLES:CAPB (w/w)	Added (mg)	Found (mg)	Recovery (%)
2:0	3.000	3.001	100.03
2:1	3.000	2.996	99.87
1:1	3.000	2.886	96.20
2:3	3.000	2.697	89.91

3.1.2. Model Liquid Detergent

A model sample of a liquid hand-dishwashing detergent was investigated, which contained 11.80 % SLES (Texapon N 70, Cognis) as an anionic surfactant and 4 % CAPB (Rokamina K30, PCC Rokita) as an amphoteric surfactant. Potentiometric titrations were performed at a preset *p*H, using DMIC as a titrant (c = 2 mM) and the HTA-TPB electrode for the determination of the end-point. The titrations were performed in the *p*H range of 1 to 10. The titration curves and their derivatives are shown in Figure 3. The results obtained are shown in Table 3.

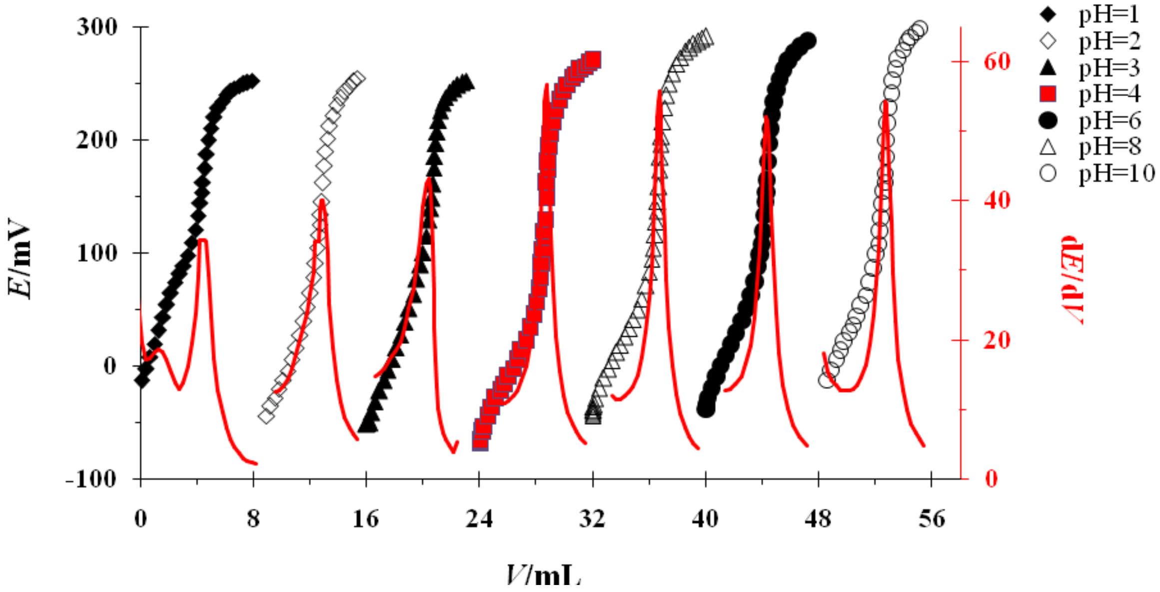

Figure 3. Titration curves with their derivatives corresponding to model samples of a liquid hand-dishwashing detergent containing SLES and CAPB. The titration curves were obtained by using DMIC as a titrant (c = 2 mM) and the HTA-TPB electrode for the determination of the end-point.

Table 3. Results of the potentiometric titration of a model samples of a liquid hand-dishwashing detergent containing SLES (11.80 %) and CAPB (4 %) in the *p*H range of 1-10.

*p*H	SLES (%)			Recovery (%)
	Expected	Found*	RSD (%)	
1	11.80	10.91	±2.14	92.46
2	11.80	11.34	±1.32	96.10
3	11.80	11.60	±0.82	98.31
4	11.80	11.76	±0.35	99.66
6	11.80	11.90	±0.52	100.85
8	11.80	11.97	±0.48	101.44
10	11.80	11.98	±0.62	101.53

* Average of 5 determinations

Below *p*H 4, the recovery decreased to 92.46 % (measured for *p*H 1) because of the protonation of CAPB in acidic solutions. Slightly increased recoveries were obtained above *p*H 5 because of the weak anionic character of CAPB in neutral or basic solutions.

3.2.Titrations of Commercial Products

Liquid detergents (liquid hand-dishwashing detergents and liquid color detergents) and personal care products (shampoos, foam baths and shower gels) were investigated.

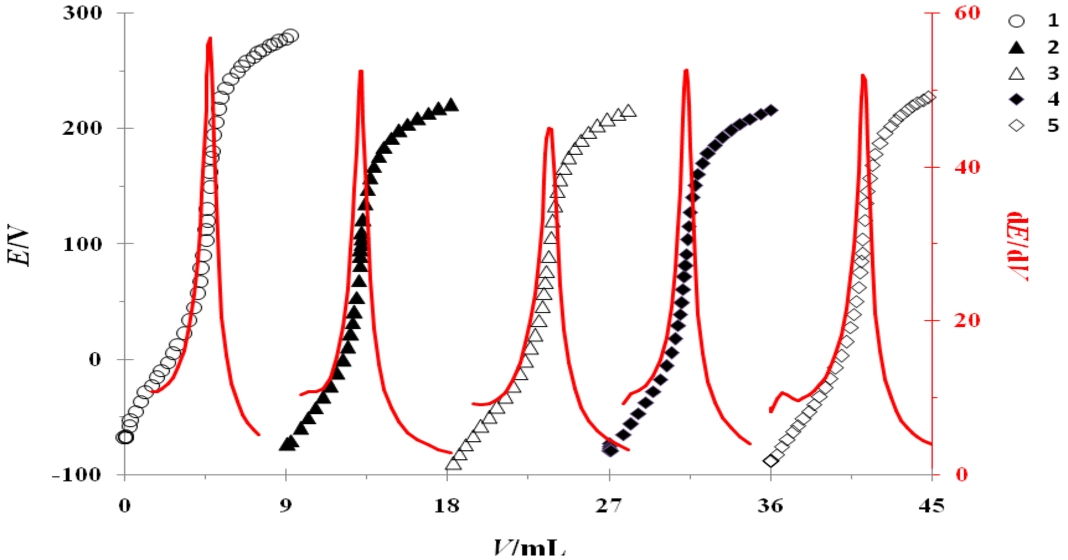

Figure 4. Titration curves with their derivatives for commercial products containing AS and amphoteric surfactants (1 – liquid hand-dishwashing detergent, 2 – liquid color detergent, 3 – shampoo, 4 – foam bath, 5 – shower gel). The titration curves were obtained by using DMIC (*c* = 2 mM) as a titrant and the HTA-TPB surfactant sensor as an indicator.

For all four detergents analyzed, the declared quantity of AS and amphoteric surfactants were 5-15 % and < 5 %, respectively. For personal care products, the AS and amphoteric surfactants were declared without limits, except for sample 6 (a shampoo) in which only the anionic surfactant was declared.

The commercial products were analyzed with preset *p*H values of 2, 4 and 10. The results are shown in Table 4 and in Figure 4. The recovery was calculated from the results obtained at *p*H 4, with the assumption that these results accurately determined the AS content of the analyzed commercial products. The mass ratio (%) of all analyzed products was based on the molecular weight of SLES (376.48).

Table 4. Results of the potentiometric titration of commercial products containing AS and amphoteric surfactants.

Sample		**Sample No.**	**ANIONIC SURFACTANT ***								
			*p*H=2			*p*H=4			*p*H=10		
			%	mmol/100g	Recovery (%)	%	mmol/100g	RSD (%)	%	mmol/100g	Recovery (%)
DETERGENT	Liquid hand-dishwashing detergent	1	6.53	17.34	93.55	6.98	18.54	0.29	7.15	18.99	102.44
		2	13.62	36.18	96.87	14.06	37.35	0.11	14.22	37.77	101.14
	Liquid color detergent	3	8.42	22.37	93.45	9.01	23.93	0.47	9.24	24.54	102.55
		4	8.14	21.62	92.50	8.80	23.37	0.35	9.53	25.31	108.30
PERSONAL CARE PRODUCTS	Shampoo	5	13.64	36.23	96.33	14.16	37.61	0.72	14.34	38.09	101.27
		6**	13.12	34.85	99.32	13.21	35.09	0.60	13.32	35.38	100.83
	Foam bath	7	10.27	27.28	96.70	10.62	28.21	0.44	0.75	28.55	101.22
		8	12.35	32.80	97.47	12.67	33.65	0.57	12.80	34.00	101.03
	Shower gel	9	7.30	19.39	94.19	7.75	20.59	0.33	7.75	21.12	102.58
		10	8.14	21.62	91.87	8.86	23.53	0.70	8.86	24.49	104.06

* Average of 3 determinations

** Sample 6 contained only anionic surfactants.

For the determination at *p*H 2, the recovery of AS in the products containing less than 10 % AS was less than 95 % (91.87 - 94.19 %). For products containing more than 10 % AS, the recovery was more than 95 % (96.33 - 97.47 %) because of the amphoteric surfactant influenced the accuracy of the AS determination less compared to the products with more than 10 % AS. However, the recovery for sample 6 was 99.32 % because it lacked amphoteric surfactants.

For the determination at *p*H 10, the recovery of AS in the products containing more than 10 % AS was less than 102 % (100.83 - 101.27 %), whereas the recovery of AS in the products containing less than 10 % AS was more than 102 % (102.44 - 104.06 %). However, for sample 4 (a liquid color detergent), the recovery was 108.30 % because of the presence of soap in the formulation (titratable at *p*H 10) together with AS (titratable in the broad *p*H range of 1 to 11) and amphoteric surfactants that have an anionic character at a higher *p*H.

4. CONCLUSIONS

A surfactant sensor composed of hexadecyltrioctadecylammonium-tetraphenylborate (HTA-TPB) as an electroactive material and *o*-nitrophenyl octyl ether (*o*-NPOE) as a plasticizer was successfully used as a detection agent for the potentiometric determination of anionic surfactants (SLES) in the presence of amphoteric surfactants (CAPB).

Amphoteric surfactants may exhibit cationic properties at low *p*H values and anionic properties at high *p*H values; thus, the exact titrimetric determination of AS in the presence of amphoteric surfactants is strongly *p*H dependent. In conclusion, the determination of SLES in model solution containing SLES and CAPB was most accurate at *p*H 4. Additionally, the accuracy of the SLES determination also decreased with an increasing CAPB content. A significant interfering effect of CAPB on the SLES determination was observed when the SLES:CAPB ratio was greater than 1:1. The method was tested and exhibited satisfactory accuracy with model liquid detergent containing SLES and CAPB and commercial products containing AS and amphoteric surfactant.

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