



Simultaneous potentiometric determination of cationic and ethoxylated nonionic surfactants in liquid cleaners and disinfectants

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ABSTRACT

A sensitive potentiometric surfactant sensor based on a highly lipophilic 1,3-didecyl-2-methylimidazolium cation and a tetraphenylborate (TPB) antagonist ion was used as the end-point detector in ion-pair potentiometric surfactant titrations using sodium TPB as a titrant. Several analytical and technical grade cationic and ethoxylated nonionic surfactants (EONS) and mixtures of both were potentiometrically titrated.

The sensor showed satisfactory analytical performances within a pH range of 3–10 and exhibited satisfactory selectivity for all CS and EONS investigated. Ionic strength did not influence the titration except at 0.1 M NaCl, in which a slight distortion of the second inflexion corresponded with the nonionic surfactant.

Two-component combinations of four CS and three EONS were potentiometrically titrated using the sensor previously mentioned as the end-point detector. The quantities of the surfactants varied between 2 and 6 μmol for CS and 2.50 and 7.50 μmol for EONS. The known addition methodology was used for determination of the surfactant with considerably lower concentration in the mixture.

Three commercial products containing cationic surfactants as disinfectants and nonionic surfactants were potentiometrically titrated, and the results for both type of surfactants were compared with those obtained with standard conventional methods.

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1. Introduction

Cationic surfactants (CS) account for only 5–6% of the total surfactant production. In spite of that, they are widely used in industrial, disinfectant, cleaning, cosmetic and pharmaceutical products due to their antimicrobial, bactericidal, anticorrosion, antistatic, softening and emulsifying properties [1]. CS are commonly known as environmental pollutants [2]. Because a large amount of cationic surfactants are produced and used frequently, it is very important to precisely determine their concentrations in the environment. CS have usually been determined by two-phase titration [3]. However, this technique had many disadvantages, such as interferences in strongly colored and turbid samples and the use of a toxic, carcinogenic solvent. The use of surfactant-sensitive electrodes as indicators in potentiometric surfactant titration overcomes these limitations. Potentiometric titrations use attractions between oppositely charged ions (ion-pair formation). Due to the increasing use of CS, considerable interest for the application of cationic surfactant-sensitive electrodes has been seen in recent years [4–9].

Nonionic surfactants account for 35% of the total surfactant production, and they are the second highest surfactant in terms of worldwide surfactant consumption. They possess specific physicochemical properties that make them particularly suited for use in many fields of research and technology. As surface active compounds, they are widely used in consumer products, e.g., laundry detergents, cleaning and dishwashing agents and personal care products [10]. Nonionic surfactants are especially important in cleaning and disinfection agents that contain CS as disinfectants, because of the incompatibility of the CS with anionic surfactants.

It is very important to accurately determine the presence of nonionic surfactants because they may be found anywhere in the environment due to their chemical properties. Potentiometric determination of EONS is based on the formation of TPB salts of pseudocationic complexes of nonionic surfactants with some metal cations, mostly barium. These complexes are often used as sensing materials in EONS-sensitive electrodes [11–16]. Nonionic surfactant sensors can be modified with PVC molecular sieves, which enable the independent determination of homologous polyethoxylated nonylphenols [17–19]. Potentiometric flow injection analysis was also used for EONS determination [20,21].

It is well known that mixed surfactant systems, such as cationic and nonionic surfactants, have the ability to provide better performance when compared to single surfactant systems [22]. Most

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commercial products are composed of more than one type of surfactants so that high-quality products can be manufactured. Generally, mixtures of cationic and nonionic surfactants are determined mainly by chromatographic methods, which are usually very complicated [23–30]. It is difficult to develop efficient chromatographic techniques to separate various surfactant mixtures and sensitive detection methods for all of the different types of surfactants. In addition to chromatographic methods, mixtures of cationic and nonionic surfactants can be determined by other techniques. The principal surfactant constituents in shampoos and liquid soaps can be determined directly, simultaneously and rapidly in undiluted samples by attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy in the middle infrared region in combination with simple chemometrics [31]. Also, mixtures of cationic and nonionic surfactants absorbing in the UV region were determined quantitatively by capillary zone electrophoresis [32] and by ion-association titration in two steps [33].

In this study, a PVC-plasticized liquid type surfactant-sensitive electrode was prepared, which used 1,3-didecyl-2-methylimidazolium-tetraphenylborate (DMI-TPB) as a ion-pair sensing element and bis(2-ethylhexyl) phthalate (DOP) as a plasticizer in membrane. DMI-TPB ion-pair was successfully used as a sensing material in potentiometric sensor used for determination of anionic [34,35] and cationic [8] surfactants. Its main advantage is high stability, very low solubility product constant which enabled a high sensitivity and high potential changes in the inflexion compared to the other ion-pairs described [11–16]. DOP was selected as a plasticizer because of its good performances obtained in previous investigations, when it was used in titrations and investigations of the nonionic surfactants [13]. The DMI-TPB sensor was applied for potentiometric titration of commonly used pure and technical grade cationic and nonionic surfactants mixtures as well as for surfactant mixtures in several commercial cleaning and disinfection agents.

2. Experimental

2.1. Reagents and materials

The following surfactants were used.

Analytical grade surfactants: Triton X-100, octylphenol decaethylene glycol ether, C_8E_{10} , $M_r = 647$, 10 EO groups (Merck, Germany); 1,3-didecyl-2-methylimidazolium chloride (DMIC, Fluka, Switzerland); hexadecyltrimethylammonium bromide (CTAB, Fluka, Switzerland); Hyamine 1622, benzethonium chloride, diisobutylphenoxyethoxyethyl dimethylbenzylammonium chloride (Fluka, Switzerland); cetylpyridinium chloride (CPC, Merck, Germany).

Technical grade nonionic surfactants: Genapol T 080, polyethylene glycol fatty alcohol based, C_{16}/C_{18} , $M_r = 613$, 8 EO groups; Genapol T 110, polyethylene glycol fatty alcohol based, C_{16}/C_{18} , $M_r = 745$, 11 EO groups (all from Clariant, Germany).

Sodium TPB (Fluka, Switzerland) solution (2.5 mM) was used as the titrant. A barium chloride (Fluka, Switzerland) solution (0.2 M) was used to form a pseudoionic complex in potentiometric titrations. All aqueous solutions were prepared with salts of the analytical grade using deionized water.

2.2. Sensor

The DMI-TPB sensor contained a 1,3-didecyl-2-methylimidazolium-tetraphenylborate ion-exchange complex, which was prepared by adding a sodium TPB solution to a 1,3-didecyl-2-methylimidazolium chloride solution. The resultant white precipitate was extracted with dichloromethane and dried with

anhydrous sodium sulfate. After evaporation and recrystallization from a 1:1 mixture of diethyl ether and methanol, the isolated ion-exchange complex was used for the preparation of the PVC based membrane plasticized with bis (2-ethylhexyl) phthalate (DOP). Detailed explanation of the preparation of DMI-TPB ion-exchange complex have been described previously [34]. Sodium chloride (1 M) was employed as the internal filling solution. A silver/silver (I) chloride reference electrode (Metrohm, Switzerland) with a sodium chloride electrolyte solution (2 M) was used as a reference. Lifetime of the sensor was more than three months by daily application.

2.3. Apparatus

An all-purpose titrator, 808 Titrand (Metrohm, Switzerland), combined with a Metrohm 806 Exchange unit (Metrohm, Switzerland) was used to dose the potentiometric titrations. The solutions were magnetically stirred during titrations using an 801 titration stand (Metrohm, Switzerland).

2.4. Titration conditions

Depending on the sample nature and the expected surfactant concentrations, between 20 and 80 mL of titration solution was used. Variable amounts of cationic and nonionic surfactant solution were used with the addition of 10 mL of a $BaCl_2$ solution (0.2 M).

All measurements and titrations were performed at room temperature using a magnetic stirrer without adjustment for ionic strength and pH. The titrator was programmed to work in DET (dynamic equivalent point titration) Mode with a signal drift of 5 mV/min and an equilibrium time of 120 s. The wait time before the start of titration varied between 30 and 60 s, depending on the sample nature and surfactant concentration.

3. Results and discussion

3.1. Potentiometric titration

The titration was carried out in one step. The anionic titrant (TPB) reacted first with the CS:



and afterward with the pseudocationic complex, which consisted of EONS and ionic barium formed by the addition of barium chloride before the titration:



More simply, the above equation can be written as follows:



where $L = EONS$.



The difference of 3–4 pK_s units between the solubility product values of both of the TPB ion associates (Eqs. (1) and (4)) caused the appearance of two distinct inflexions at the titration curve. The first inflexion related to the surfactant that formed with less soluble TPB ion-pair complex (with a lower solubility product value). Usually, it was the CS.

3.1.1. Titration of pure and technical grade surfactant mixtures

Sodium TPB used as a titrant reacted first with the CS^+ and was accompanied by the formation of a water insoluble (1:1) ion-pair $CS^+ TPB^-$ (Eq. (1)), which solubility product is defined as:

$$K_{S1} = a_{CS^+} \cdot a_{TPB^-} \quad (5)$$

where a_{CS^+} and a_{TPB^-} are activities of the corresponding ions.

The response of the membrane sensor assembly used toward CS^+ is given by the Nernst equation:

$$E_{CS^+} = E_{CS^+}^0 + S_{CS^+} \cdot \log a_{CS^+} \quad (6)$$

where $E_{CS^+}^0$ is the constant potential term, S_{CS^+} is the sensor slope, and a_{CS^+} is the activity of the surfactant cation.

Before the first equivalence point, the change (decrease) in the sensor potential responded to the change (decrease) in the CS concentration as shown in Eq. (6).

By combining Eqs. (5) and (6) and after rearrangement, the following sensor response is obtained:

$$E_{CS^+} = \text{const}_{CS^+} - S_{CS^+} \cdot \log a_{TPB^-} \quad (7)$$

where $\text{const}_{CS^+} = E_{CS^+}^0 + S_{CS^+} \cdot \log K_{S1}$.

After the first equivalence point (the point at which all the CS was precipitated), the TPB titrant reacted with the pseudocationic complex of EONS and ionic barium according to Eq. (4).

The solubility product of this precipitate is:

$$K_{S2} = a_{BaL_x^{2+}} \cdot (a_{TPB^-})^2 \quad (8)$$

TPB was a component of the ion-exchange complex used as the sensing material in the sensor membrane. Therefore, the sensor responded to TPB according to the following equation:

$$E_{TPB^-} = E_{TPB^-}^0 - S_{TPB^-} \cdot \log a_{TPB^-} \quad (9)$$

where $E_{TPB^-}^0$ is the constant potential term, S_{TPB^-} is the slope, and a_{TPB^-} is the activity of the TPB anion. From Eqs. (8) and (9) and after rearrangement, the following sensor response is obtained:

$$E_{TPB^-} = \text{const}_{TPB^-} + S_{TPB^-} \cdot \log (a_{BaL_x^{2+}})^{1/2} \quad (10)$$

where $\text{const} = E_{TPB^-}^0 - S_{TPB^-} \cdot \log K_{S2}^{1/2}$

Eq. (10) shows that after the first equivalence point was reached, and after the reaction of TPB with the pseudocationic complex of EONS and ionic barium, the concentration of the latter decreased, which resulted in a further decrease of the sensor potential, E .

After the second equivalence point (the point at which all the pseudocationic EONS complexes were precipitated), further addition of TPB titrant caused further decreases of the sensor potential, E (Eq. (9)).

Eqs. (7) and (10) show that the magnitude of the inflexion at the equivalence point was strongly dependent on the value of the solubility product of the ion-pair. The lower K_S value of the ion-pair formed during titration caused a higher potential change at the equivalence point, which resulted in a more sensitive surfactant determination. The insufficient difference in solubility product constants of the ion-associates described by Eqs. (1) and (4) results with the absence of two distinctive inflexions and thus differential titration of the both surfactants, which is the main limitation of the proposed method.

The standard TPB solution was used as the titrant in the titration of cationic and EONS mixtures, which formed water-insoluble (1:1) complexes. Four CSs (Hyamine 1622, CPC, CTAB and DMIC) and 3 nonionic surfactants (Genapol T 080, Genapol T 110 and Triton X-100) were used for the investigations described in this study. Both Genapol surfactants are often used in detergent formulations, whereas Triton X-100 was selected because of its analytical importance as a reference EONS in the official method for EONS determination in effluents [36] and its application in biochemical laboratories to make eukaryotic cell membranes permeable and to solubilize membrane proteins in their native states [37–40].

All the two-component combinations of a CS and an EONS were potentiometrically titrated using the sensor previously mentioned

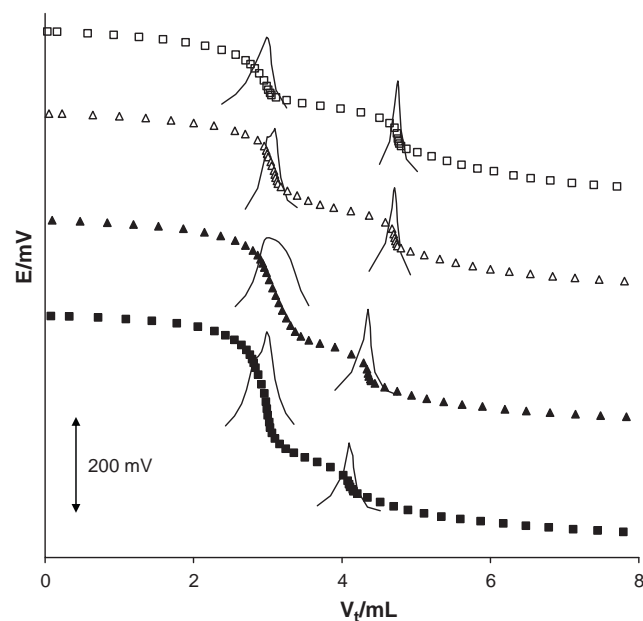


Fig. 1. Titration curves and their first derivatives of the Genapol T 080 ($c=2.0$ mM) mixture with various cationic surfactants ($c=2.5$ mM) using sodium TPB ($c=2.5$ mM) as a titrant and a DMI-TPB sensor as the end-point detector. In this and in the next figures, some curves are displaced vertically for clarity (■ DMIC + Genapol T 080; ▲ CPC + Genapol T 080; △ CTAB + Genapol T 080; □ Hyamine + Genapol T 080).

as the end-point detector. The corresponding potentiometric titration curves are shown in Figs. 1–3. The equivalence points for all potentiometric titrations were calculated from the derivative curves.

The titration curves of the Genapol surfactants mixture with each CS exhibited well-resolved inflexions, which enabled accu-

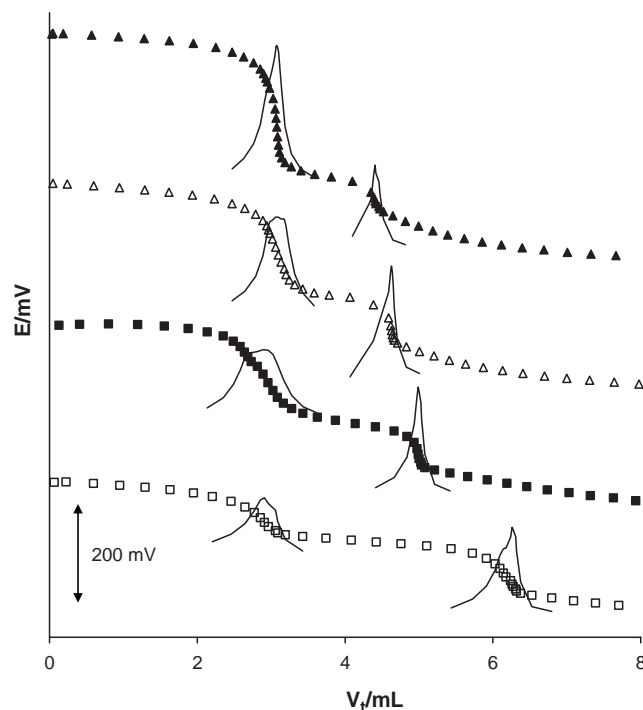


Fig. 2. Titration curves and their first derivatives of the Genapol T 110 ($c=1.5$ mM) mixture with various cationic surfactants ($c=2.5$ mM) using sodium TPB ($c=2.5$ mM) as a titrant and a DMI-TPB sensor as the end-point detector (□ Hyamine + Genapol T 110; ■ DMIC + Genapol T 110; ▲ CPC + Genapol T 110; △ CTAB + Genapol T 110).

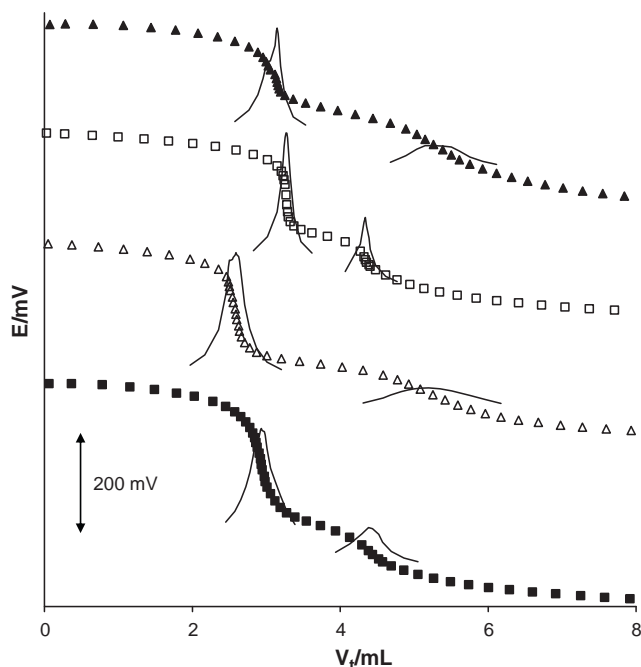


Fig. 3. Titration curves and their first derivatives of the Triton X-100 ($c = 2.0 \text{ mM}$) mixture with various cationic surfactants ($c = 2.5 \text{ mM}$) using sodium TPB ($c = 2.5 \text{ mM}$) as a titrant and a DMI-TPB sensor as the end-point detector (■ DMIC + Triton X-100; △ CTAB + Triton X-100; □ Hyamine + Triton X-100; ▲ CPC + Triton X-100).

rate end-point determinations (Figs. 1 and 2). Titration curves of the Triton X-100 mixture with CS revealed strong inflexions for each CS (the first inflexion). The magnitude of the second inflexion (related to Triton X-100) varied depending on the nature of the CS. The titration of the mixture of Triton X-100 with DMIC and CPC exhibited a well-defined inflexion, whereas its titration with two other CS revealed less pronounced inflexions. These equivalence points were reliably calculated from the derivative curves using an extension of the least-squares regression formalism of the Savitzky–Golay method developed by Barak [41]. Statistical testing of the polynomial degree was conducted using an adaptive-degree polynomial filter, which selected the lowest polynomial degree that was statistically justifiable.

The recovery statistics of the potentiometric determinations of the two-component combinations of each CS and EONS are shown in Table 1. The quantities of the surfactants investigated varied between 2.50 and 7.50 μmol for CS and 2.00 and 6.00 μmol for EONS.

Errors appeared when the ratio of titrant consumptions for titration of a particular surfactant in the mixture exceeded the value of

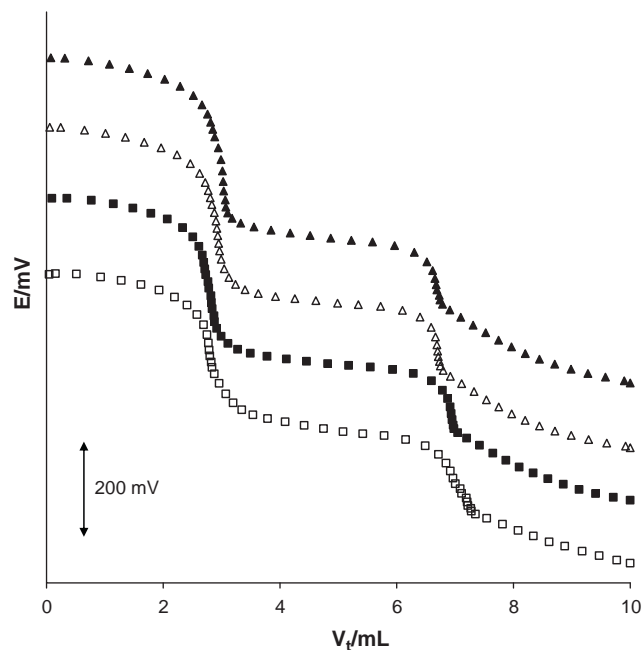


Fig. 4. The effect of ionic strength on the shape of the titration curves by titration of the mixtures of CPC ($c = 2.5 \text{ mM}$) and Genapol T 080 ($c = 2.0 \text{ mM}$) using sodium TPB ($c = 2.5 \text{ mM}$) as a titrant and a DMI-TPB sensor as the end-point detector ($c(\text{NaCl}) = \blacktriangle 0.01 \text{ M}$, $\triangle 0.02 \text{ M}$, $\blacksquare 0.05 \text{ M}$, $\square 0.1 \text{ M}$).

3:1 (results not shown). These errors were significantly reduced by performing a preliminary titration and a subsequent known addition of the surfactant with lower titrant consumption.

3.1.2. Interferences

3.1.2.1. Influence of the ionic strength. To investigate the effect of ionic strength on the shape of titration curves, mixtures of CPC (cationic surfactant) and Genapol T 080 (nonionic surfactant) containing different concentrations of NaCl (0.01 M, 0.02 M, 0.05 M, 0.1 M) were titrated. No distortions of the titration curves at the inflexions and no significant shifts of the end-point volumes were observed at NaCl concentrations of 0.01, 0.02 and 0.05 M (Fig. 4). Slight distortion of the second inflexion (nonionic surfactant) appeared at a concentration of 0.1 M NaCl, i.e., at an NaCl concentration more than 750 times higher than the nonionic surfactant.

3.1.2.2. Influence of pH. The stability of the sensor response was investigated over a wide pH range to simulate the practical titration conditions of different formulated products of varying acidity

Table 1

Recovery statistics of the potentiometric determination of two-component combinations of each CS and EONS investigated.

Mixture no.	CS	Added (μmol)	Found (μmol)	Recovery ^a (%)	EONS	Added (μmol)	Found (μmol)	Recovery ^a (%)
1	CPC	7.50	7.46	99.5	Genapol T 080	6.00	5.77	96.2
2	CTAB	7.50	7.56	100.8	Genapol T 080	6.00	5.81	96.8
3	DMIC	7.50	7.64	101.8	Genapol T 080	2.00	1.92	96.1
4	Hyamine	7.50	7.41	98.8	Genapol T 080	6.00	5.90	98.3
5	CPC	2.50	2.60	103.9	Genapol T 110	4.50	4.45	98.9
6	CTAB	7.50	7.55	100.6	Genapol T 110	4.50	4.51	100.1
7	DMIC	7.50	7.33	97.7	Genapol T 110	4.50	4.52	100.5
8	Hyamine	7.50	7.61	101.5	Genapol T 110	4.50	4.44	98.7
9	CPC	7.50	7.72	102.9	Triton X-100	6.00	5.97	99.5
10	CTAB	7.50	7.84	104.5	Triton X-100	6.00	5.72	95.3
11	DMIC	7.50	7.34	97.8	Triton X-100	2.00	2.05	102.3
12	Hyamine	7.50	7.67	102.2	Triton X-100	6.00	6.10	101.6

^a Average of 5 determinations.

Table 2

Results of three commercial liquid cleaning and disinfection agents obtained by potentiometric titration using a DMI–TPB sensor and sodium tetraphenylborate (5×10^{-3} M) as a titrant compared with results obtained by two-phase titration for cationic and the gravimetric method for nonionic surfactants.

Sample	Surfactant content			
	Cationic surfactant (%)		Nonionic surfactant (%)	
	DMI–TPB electrode ^a	Two-phase titration ^b	DMI–TPB electrode ^a	Gravimetric method ^b
Product A	1.02 ± 0.03	1.00	1.42 ± 0.04	1.60
Product B	5.04 ± 0.07	4.95	7.58 ± 0.09	6.85
Product C	4.44 ± 0.05	4.50	4.89 ± 0.07	4.46

^a Average of 5 determinations $\pm \sigma_{N-1}$.

^b Average of 3 determinations.

and alkalinity. The investigations were performed in solutions containing CPC as the CS and Genapol T 080 as the nonionic surfactant. The pH values were adjusted with NaOH and H₂SO₄ (1 M, 0.1 M and 0.01 M, for both NaOH and H₂SO₄). There were no significant changes in the shapes of titration curves within the pH range of 3–10, which indicated the applicability of the sensor in strongly acidic and alkaline conditions (Fig. 5).

3.1.3. Titration of commercial products

Three commercial products containing CS as disinfectants and nonionic surfactants were potentiometrically titrated: an acidic liquid cleaner and disinfectant containing a C₉–C₁₁ oxo-alcohol with 7 EO per molecule as a nonionic surfactant, phosphoric acid and benzalkonium chloride as the disinfectant (Product A); a universal liquid agent for cleaning and disinfection containing a C₁₃–C₁₅ oxo-alcohol with 8 EO per molecule and benzalkonium chloride (Product B); and a liquid agent for cleaning and disinfection of working surfaces and food-processing equipment in foodstuff industry containing a C₉–C₁₁ oxo-alcohol with 7 EO per molecule and benzalkonium chloride (Product C).

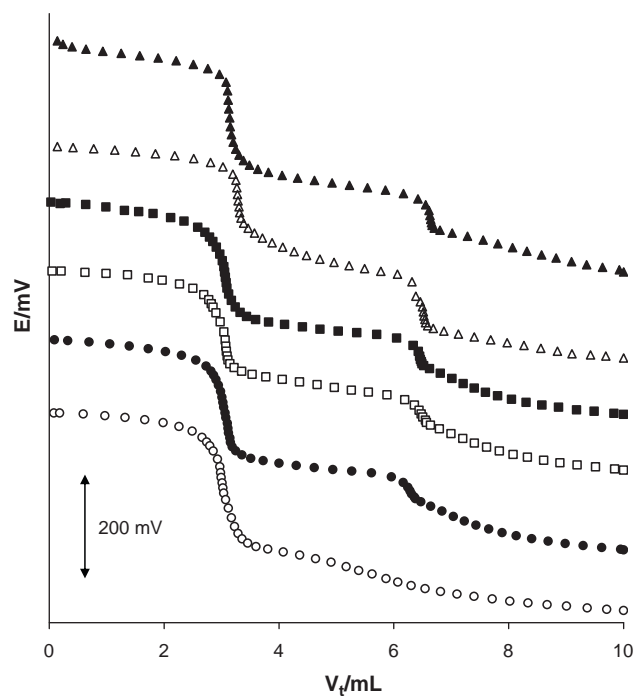


Fig. 5. The influence of pH on the shape of the titration curves by titration of the mixtures of CPC ($c=2.5$ mM) and Genapol T 080 ($c=2.0$ mM) using sodium TPB ($c=2.5$ mM) as a titrant and a DMI–TPB sensor as the end-point detector (▲ pH 3, △ pH 5, ■ pH 7, □ pH 9, ● pH 10, ○ pH 11).

Sodium TPB solution (5 mM) was used as a titrant in potentiometric titrations. Before starting titrations, 10 mL of barium chloride (0.2 M) was added, and pH values were checked and adjusted to between 3 and 9. Potentiometric titration curves for all the samples revealed an analytically usable inflexion, which enabled reliable detection of the equivalence point using the first derivative method. The results obtained were compared with those obtained with two-phase titration for CSs [42] and gravimetric methods for determination of nonionic surfactants combined with cation exchange column chromatography to separate nonionic and CSs [43] (Table 2). Titration curve and its first derivative of a liquid agent for cleaning and disinfection is presented in Fig. 6. The first inflexion point on the titration curves related usually to the amount of titrant used for CS titration because CS forms slightly soluble ion associate with TPB, which solubility product constant is several orders of magnitudes lower than that of TPB and the pseudo-cationic complex of EONS and barium ion. The calculation of the CS content (w/w) was possible only if molecular mass (MM) of CS is known. In case of the unknown MM the result can be expressed in mols of CS per mass of the product. Two different ethoxylated oxo-alcohols with different alkyl chain lengths (C₉–C₁₅) containing 7 and 8 EO groups, most frequently used in formulated products investigated, were successfully simultaneously titrated. Their quantification required the prior estimation of the corresponding experimental stoichiometric factors (mg EONS/mL NaTPB solution used as a titrant) for each EONS investigated [13].

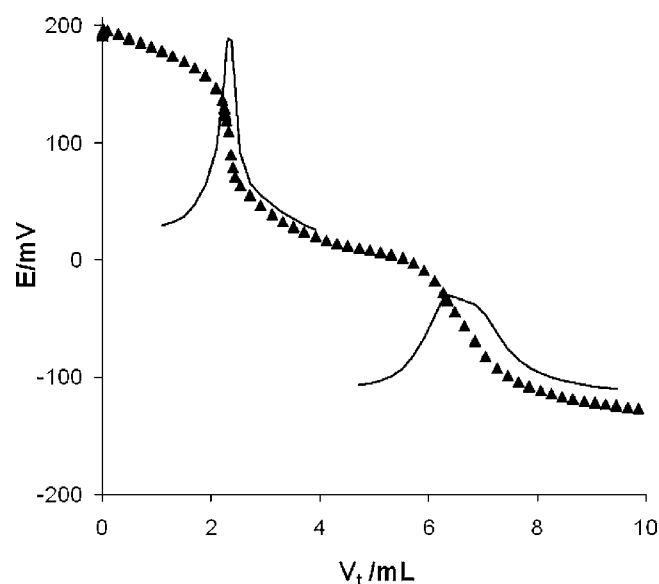


Fig. 6. Titration curve and its first derivative of a liquid agent for cleaning and disinfection containing C₁₃–C₁₅ oxo-alcohol with 8 EO per molecule and benzalkonium chloride, using sodium TPB ($c=5.0$ mM) as a titrant and a DMI–TPB sensor as the end-point detector.

4. Conclusions

A sensitive potentiometric surfactant sensor based on a highly lipophilic 1,3-didecyl-2-methyl-imidazolium cation and a TPB antagonist ion was used as the end-point detector in ion-pair surfactant potentiometric titrations.

The standard TPB solution was used as the titrant for the titration of CS and EONS mixtures, which formed water insoluble complexes. Four CSs (Hyamine 1622, CPC, CTAB and DMIC) and three nonionic surfactants (Genapol T 080, Genapol T 110 and Triton X-100) were used for the investigations.

The two-component combinations of each CS and EONS investigated were potentiometrically titrated using the sensor previously mentioned as the end-point detector. Titration curves for both Genapol surfactant mixtures with each CS exhibited well-resolved inflexions, which enabled accurate end-point determination. Titration curves of the Triton X-100 mixture with CSs exhibited strong inflexions for each CS titrated (the first inflexion). The magnitude of the second inflexion (related to Triton X-100) varied depending on the nature of the CS. The titration of the mixture of Triton X-100 with DMIC and CPC exhibited a well-defined inflexion, whereas its titration with two other CSs revealed less pronounced inflexions.

The quantities of the surfactants investigated varied between 2.50 and 7.50 μmol for CS and 2 and 6 μmol for EONS. Errors appeared when the ratio of titrant consumptions for each component in the mixture exceeded 3:1. The errors were significantly reduced by performing a preliminary titration and a subsequent known addition of the surfactant of a lower concentration to consume a titrant volume of 4–5 mL for each component in the mixture.

Ionic strength did not influence the shape of titration curves except at 0.1 M NaCl, at which point a slight distortion of the second inflexion related to the nonionic surfactant was observed. The surfactant mixtures were successfully titrated in the pH range of 3–10.

Three commercial products containing CSs as disinfectants and nonionic surfactants were potentiometrically titrated, and the results were compared to those obtained with two-phase titrations for CSs and a gravimetric method for nonionic surfactants.

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