

Potentiometric determination of anionic surfactants using a new ion-pair-based all-solid-state surfactant sensitive electrode

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Abstract

An all-solid-state surfactant sensitive electrode has been prepared, based on a teflonised graphite conducting substrate coated with plasticised PVC-membrane containing a new synthesized tetrahexadecylammonium-dodecylsulfate as anionic surfactant sensing material. The electrode exhibited Nernstian response (58.1 mV/decade) for dodecylbenzenesulfonate and a near-Nernstian response (64.2 mV/decade) for dodecylsulfate. The electrode was used as end-point indicator for potentiometric surfactant titrations. The selectivity coefficients relating to the common inorganic and organic anions have been calculated by modelling of Nikolskii–Eisenman equation. Several commercial surfactants have been also titrated. The electrode enables the titration of shorter hydrocarbon chain anionic surfactants, as well.

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1. Introduction

Among several millions metric tons of surfactants yearly produced, about 70% represent the anionic ones. Its wide use in various application areas (industrial products, household and cosmetic products, etc.) imposes the importance of quality control. Besides, the environmental impact of surfactants, as serious pollutants of aquatic systems implies the importance of adequate analytical methods for their determination.

Ionic surfactants (both anionic and cationic ones) have usually been determined by two-phase titration methods [1].

Abbreviations: DBS, dodecylbenzenesulfonate; DDMBA, dodecyltrimethylbenzylammonium; DES, dodecylethersulfate; DeS, decane-sulfonate; DIOSS, diisooctylsulfosuccinate; DS, dodecylsulfate; EDTA, ethylenediaminetetraacetic acid, disodium salt; EO, ethoxy; HTMAB, hexadecyltrimethylammonium bromide; Hy, hyamine; OS, octylsulfate; SAS, sec-alkansulfonate; SS, sulfosuccinate; TA, tetrahexadecylammonium; TPP, tripolyphosphate; TS, p-toluenesulfonate; XS, xylenesulfonate

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The main disadvantage of these methods are: the limitation of application to strongly coloured and turbid samples, the toxicity of organic chlorinated solvent used, the formation of emulsion during titration which can disturb visual end-point detection, the numerous matrix interferences, etc. Most of these limitations can be overcome by using of ion sensitive (selective) electrodes (ISEs) as indicators in potentiometric surfactant titration.

All surfactant titrations are based on so called antagonist reaction, where an ionic surfactant reacts with an oppositely charged ion (mainly surfactant, too) forming a water insoluble salt (ion-pair). Among the first electrodes used were those of coated-wire type based on ion-association complexes of quaternary ammonium cation and surfactant anion [2–4]. Ciocan and Anghel [5–7] were one of the first to perform surfactant titrations using a sensor based upon a complex of ferroin and dodecylsulfate or dodecylbenzenesulfonate. Several excellent articles [8–10] reviewed the use of different types of electrodes for surfactant analysis. Buschmann et al. [11–16] have reported further advancements in electrode design, titrant selection, etc.

The most challenging applications of surfactant analysis are in determination of low concentration levels of surfactants in environmental materials. The use of surfactant sensitive electrodes for the potentiometric determination of low concentrations of anionic surfactants has been described in several papers [17–22].

The preparation of photocurable polymer membrane selective to anionic surfactants and their application to all-solid-state ion-selective electrodes, as well as its application for the construction of ISFET sensitive to anionic surfactants used for monitoring surfactant photodegradation processes has been described [23,24]. Kovacs et al. [25] constructed an all-solid-state surfactant sensitive electrode using teflonised graphite rods coated with conducting polymer (electrochemically synthesized polypyrrole) as internal electric contact and ion-pair-based PVC membrane as sensing material.

In this paper a teflonised graphite electrode coated with plasticised PVC, containing a new synthesized ion-pair-based on a tetrahexadecylammonium cation, and dodecylsulfate as the antagonist ion (TA–DS) serving as surfactant sensing material, was described. The electrode was applied for potentiometric titration of the commonly used pure and technical grade anionic surfactants.

2. Experimental

2.1. Preparation of TA–DS ion-exchange complex

Ion-exchange complex (ion-pair) tetrahexadecylammonium dodecylsulfate (TA–DS) was prepared by dropwise addition of 10 cm³ of a hot (50 °C) 0.05 M sodium dodecylsulfate aqueous solution to 30 cm³ of a hot ethanol–water mixture (volume ratio = 2:1) containing equimolar amount of tetrahexadecylammonium bromide. The reaction mixture was heated under stirring, and at 68 °C it instantaneously became clear. By further heating upto 80 °C the white precipitate was formed. The mixture had been stirred at 80 °C until all ethanol got evaporated. After cooling the formed ion-pair, the precipitate was filtered off and thoroughly washed with water till negative reaction to bromide ion. The isolated precipitate was dried at 80 °C till constant weight and stored in desiccator.

2.2. Preparation of other ion-exchange complexes

The preparation procedure for the particular ion-pair was dependent on the nature of ionic species used, so two different procedures were used:

2.2.1. Dodecyltrimethylbenzylammonium dodecylsulfate (DDMBA–DS)

The DDMBA–DS ion-pair was obtained by dropwise addition of the of 0.1 M solution of sodium dodecylsulfate (Na–DS) to the equal amount of 0.1 M solution of dodecyltrimethylbenzylammonium (DDMBA) chloride

(Henkel–Cognis). After complete addition of Na–DS, the resulting mixture was warmed upto 50 °C and continuously stirred next 15 min. The precipitated ion-pair DDMBA–DS was filtered off and washed thoroughly with deionised water until negative reaction to halogenide ion. The resulting thoroughly washed precipitate was then dried at 105 °C till constant weight.

The analogous procedure was used for the synthesis of dodecyltrimethylbenzylammonium dodecylbenzenesulfonate (DDMBA–DBS), Hyamine dodecylsulfate (Hy–DS) and Hyamine dodecylbenzenesulfonate ion-pair (Hy–DBS). Hyamine 1622 (benzethonium chloride, diisobutylphenoxyethoxyethyltrimethylbenzyl–ammonium chloride) of reagent grade quality was supplied by Fluka.

2.2.2. Hyamine stearate

The Hyamine-stearate was obtained by dropwise addition of 1 mmol/dm³ of sodium stearate to the equal amount of 1 mmol/dm³ Hyamine solution. The reaction mixture was treated according to the same procedure described above. The solution (1 mmol/dm³) of sodium stearate was prepared by refluxing of stearic acid (Fluka) and sodium hydroxide according to the procedure described elsewhere [28].

2.3. Electrode preparations

The electrode coating mixtures were of the following composition: *o*-nitrophenyloctylether (*o*-NPOE) as plasticiser (66%), PVC of high molecular mass (33%) and ion-pair-based ion-exchange sensing material (1%). The mass of 1 g of mixture was dissolved in 20 cm³ of tetrahydrofuran. A teflonised graphite electrode [17], which served as a membrane carrier, was dipped in the coating mixture and after evaporation of the solvent, the procedure was repeated twice. Between measurements, the electrode was kept in the air. After each 2–3 h of effective work, the electrode must be reconditioned in the solution of sodium dodecylsulfate ($c = 10^{-3}$ mol/dm³). A few preliminary titrations are highly recommended as a preconditioning procedure before using the electrode as indicator in quantitative titrations. The lifetime of the electrode was several months when kept in pure surfactant solutions, but decreased when kept in more complex solutions.

2.4. Reagents and solutions

The sodium dodecylsulfate and sodium dodecylbenzenesulfonate were used for electrode response characteristics measurements and for potentiometric titrations. The standard solution ($c = 4$ mmol/dm³) of Hyamine and hexadecyltrimethylammonium bromide (HTMAB) was used as titrant.

All the above-mentioned chemicals were of reagent grade quality and supplied by Fluka, except of sodium dodecylbenzenesulfonate, which was of technical grade quality. The purification and standardization of the latter was

performed according to the procedure described elsewhere [1].

2.5. Apparatus

The electrode potential measurements (0.1 mV resolution) were performed with a microprocessor-controlled pH meter MA 5740 (Iskra, Slovenia), using the ion-pair-based potentiometric sensor described as indicator electrode, and Ag/AgCl (3 M KCl) double junction electrode (Metrohm, Switzerland) as a reference electrode. The potentiometric titrations were performed using a self-assembled computerized titration system including digital pH meter/milivoltmeter for electromotive force recording and Radiometer piston burette for titrant dosage. The volume addition reproducibility was $\pm\mu\text{L}$ and the equivalence points were determined by numeric derivation of the smoothed data. The six ion-pair-based potentiometric sensors (Hy-DBS, Hy-DS, Hy-stearate, DDMBA-DBS, DDMBA-DS and TA-DS) have been investigated, and the system TA-DS showed the superior performance. Therefore, this TA-DS sensor was used in further applications. The sensor is sensitive to both anionic surfactants as well as cationic ones [29].

2.6. Procedure

The electrode has been calibrated with standard solutions of sodium dodecylsulfate and sodium dodecylbenzenesulfonate in the range of 10^{-2} – 10^{-6} mol/dm³. The volume of solution used for titration was 20 cm³. All measurements and titrations were performed at $(25.0 \pm 0.2)^\circ\text{C}$. The titrant dosage rate was 0.07 cm³/min. The pH value during titration was controlled with glass electrode.

3. Results and discussion

3.1. Response characteristics

Electromotive force of the membrane electrode assembly dipped in the solution of anionic surfactant investigated is given by Nernst equation:

$$E = E^\circ - \text{slope} \log a(\text{SAn}^-) \quad (1)$$

where E° = formal potential, slope = Nernst slope = $2.3RT/zF$, $a(\text{SAn}^-)$ = activity of surfactant anion.

The response characteristics of TA-DS surfactant sensor in solutions of sodium dodecylsulfate and sodium dodecylbenzenesulfonate are shown in Fig. 1. The activity coefficients were calculated according to the Davies equation (an extended form of the Debye-Hückel equation). Statistical evaluation of the electrode characteristics is given in Table 1. The slope values, correlation coefficients and intercepts were calculated from the linear region of the calibration graphs on the five series of measurements using linear

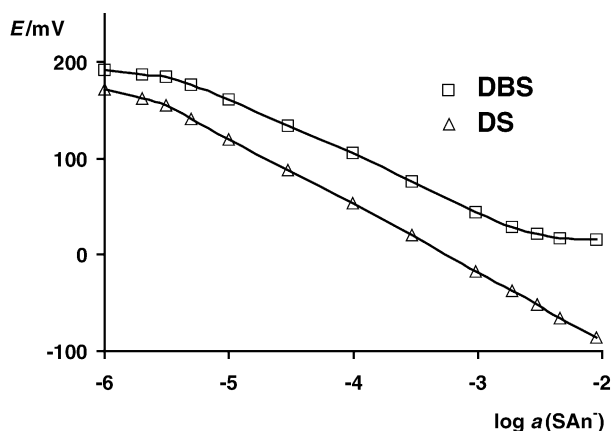


Fig. 1. Dodecylsulfate (DS) and dodecylbenzenesulfonate (DBS) response of TA-DS ion-pair-based surfactant sensor.

regression analysis. Detection limits were estimated according to the IUPAC recommendations [26]. The electrode investigated showed Nernstian response (58.1 mV/decade) between $5 \mu\text{mol/dm}^3$ and 2mmol/dm^3 for dodecylbenzenesulfonate and a near-Nernstian response (64.2 mV/decade) between $3 \mu\text{mol/dm}^3$ and 10mmol/dm^3 for dodecylsulfate. It can be seen that electrode exhibits linear response for the dodecylsulfate anion even above critical micellar concentration (CMC).

Practical response time of the electrode investigated was within 30 s, except for the lowest concentrations ($<10 \mu\text{mol/dm}^3$), where it was nearly 1 min. Agreement between several electrode-coating procedures was satisfactory concerning analytical performances of the electrodes.

The other sensors investigated, revealed slightly inferior analytical characteristics, compared with TA-DS based electrode and were not further considered for response characteristics measurements and for potentiometric titrations.

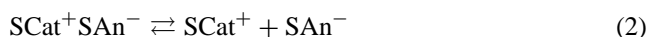
3.2. Potentiometric titration

The main application of the electrodes described was for indication of the end-point in ion-pair surfactant potentiometric titrations. Anionic surfactant (SAn^- = analyte determined) reacts during titration with cationic surfactant (SCat^+ = titrant) accompanied by forming a water insoluble (1:1)

Table 1
Response characteristics of TA-DS based membrane selective to the anionic surfactants given together with $\pm 95\%$ confidence limits

Parameters	Anionic surfactants	
	Dodecylsulfate	Dodecylbenzenesulfonate
Slope (mV/decade)	64 ± 1	58 ± 2
Intercept (mV)	-196 ± 4	-214 ± 7
Correlation coefficient (r)	0.9995	0.9992
Detection limit ($\mu\text{mol/dm}^3$)	2.4	3.4
Useful conc. range ($\mu\text{mol/dm}^3$)	3–10000	5–2000

ion-pair $\text{SCat}^+\text{SAn}^-$ (ion-exchange or ion-pair complex):



For the above equilibrium solubility product is defined as

$$K_{\text{sp}} = a(\text{SCat}^+) \cdot a(\text{SAn}^-) \quad (3)$$

where $a(\text{SCat}^+)$ and $a(\text{SAn}^-)$ are activities of the corresponding surfactant ions.

Before the equivalence point, the change (increase) of electrode potential responded to the change of anionic surfactant concentration as followed by the Eq. (1). After the equivalence point (all the anionic surfactant is precipitated), the increase of cationic surfactant concentration in solution is evident.

From Eq. (3) $a(\text{SAn}^-) = K_{\text{sp}}/a(\text{SCat}^+)$, and after inserting it into Eq. (1), the following electrode response is obtained:

$$E = E^\circ - \text{slope} \log \frac{K_{\text{sp}}}{a(\text{SCat}^+)} \quad (4)$$

which after rearrangement gives:

$$E = \text{const} + \text{slope} \log a(\text{SAn}^-) \quad (5)$$

where $\text{const} = E^\circ + \text{slope} \log K_{\text{sp}}$

From Eq. (5) it follows, that after equivalence point the electrode responds to the change of cationic titrant (cationic response). Further addition of cationic titrant after equivalence point causes further increase of electrode potential E .

The standard solutions of Hyamine 1622 and HTMAB ($c = 4 \text{ mmol/dm}^3$) were used as titrants in the determination of anionic surfactants forming the water insoluble (1:1) complexes. The four sodium salts of analytical grade anionic surfactants (dodecylsulfate, dodecylbenzenesulfonate, *n*-octylsulfate and decansulfonate) have been titrated potentiometrically using a new TA–DS membrane electrode as surfactant sensor for end-point determination. The resulting potentiometric titration curves are shown in Fig. 2. The statistical parameters of these titrations are given in Table 2.

The shorter hydrocarbon chain in anionic surfactants, due to their lower solubility, are usually more difficult to titrate (by both potentiometric and by two-phase titration method). The use of TA–DS based surfactant electrode as indicating one enables the potentiometric titration even of those anionic surfactants (e.g. *n*-octylsulfate, decansulfonate). Owing to increased solubility of ion-pairs formed during titration with cationic titrant, the titration is only possible at the higher

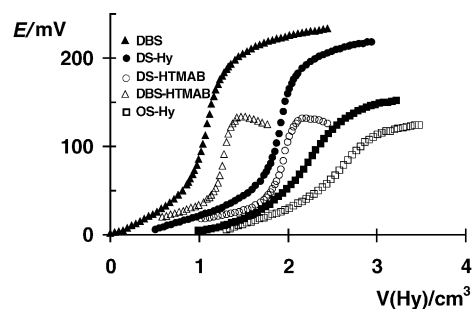


Fig. 2. Titration curves of several analytical grade anionic surfactants with TA–DS surfactant sensor and Hyamine (Hy) and HTMAB as titrants (DS = dodecylsulfate; DBS = dodecylbenzenesulfonate; OS = octylsulfate; DeS = decansulfonate). Here and in further figures some curves are displaced laterally or vertically for clarity.

concentrations of titrand and titrant. The titrand (analyte) concentration level of all the anionic surfactants investigated was $c = 0.4 \text{ mmol/dm}^3$, except for *n*-octylsulfate (OS) and decansulfonate (DeS), where it was 4 mmol/dm^3 . The titrant (Hyamine) concentration for the latter was 40 mmol/dm^3 . The titration curves obtained with Hyamine solution exhibited regular defined and sharp inflexion points with high potential jump (170–200 mV) at the equivalence point, except for *n*-octylsulfate and decansulfonate, where the potential jump was between 80 and 100 mV. The use of HTMAB as titrant gave irregular shaped titration curves after equivalence point and lower potential jump at the equivalence point.

The new TA–DS surfactant electrode has been also tested for titration of several frequently used commercial (technical grade) anionic surfactants (their sodium salts): dodecylsulfate (DS), dodecylbenzenesulfonate (DBS), dodecylethersulfate (DES), *sec*-alkansulfonate (SAS), diisooctylsulfosuccinate (DIOSS) and palmitate (Fig. 3). The results of these determinations were compared with standard, internationally verified, two-phase titration method (see Table 3).

The equivalence points by all titrations have been calculated from the derivative curves. The slightly higher noise level in the region of the equivalence point, by titrating some technical grade surfactants, has been digitally filtered by using multiple point moving parabola, before calculating the first derivative values. This can be easily calculated by using Microsoft Excel spreadsheets or some other mathematical software packages.

Table 2

Results of potentiometric titrations of some analytical grade anionic surfactants using Hyamine as titrant and TA–DS sensor as indicator

Surfactant investigated	c (taken) (μM)	c^{a} (found \pm standard deviation) (μM)	Recovery (%)	Relative standard deviation (%)
Sodium dodecylsulfate	6.00	5.99 ± 0.02	99.8	0.33
Sodium dodecylbenzenesulfonate	6.80	6.79 ± 0.04	99.9	0.52
Sodium <i>n</i> -octylsulfate	50.00	49.7 ± 0.7	99.4	1.34
Sodium decansulfonate	50.00	49.7 ± 0.8	99.4	1.55

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

Table 3

Results obtained by potentiometric titrations of technical grade anionic surfactants using Hyamine as titrant and TA–DS sensor as indicator, compared with two-phase titration method

Surfactant	Potentiometric titration		Two-phase titration w^a (active matter) (%)
	w^a (active matter \pm standard deviation) (%)	Relative standard deviation (%)	
Sodium dodecylsulfate	88.5 ± 0.7	0.8	89.2
Sodium dodecylbenzensulfonate	90.7 ± 0.9	1.0	91.3
Sodium laurylethersulfate	29.6 ± 0.3	1.0	30.3
Sodium sec-alkansulfonate	59.7 ± 0.6	1.0	61.1
Sodium diisooctylsulfosuccinate	45.0 ± 0.6	1.3	45.7
Sodium palmitate	93.0 ± 0.9	1.0	92.6

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

3.3. Interferences

3.3.1. The influence of pH

The electrode potential stability has been investigated in a wide pH range, simulating in this way the practical titration conditions of different more or less acidic or alkaline formulated products. The investigations were performed in the solutions of sodium dodecylsulfate and sodium dodecylbenzensulfonate at two concentration levels: 0.4 and 4 mmol/dm³. The pH values were adjusted with solutions of NaOH and H₂SO₄ ($c = 1, 0.1$ and 0.01 M, respectively). The surfactant solutions investigated contained 0.1 mol/dm^3 of Na₂SO₄ providing the measurements at constant ionic strength. The electrode potential readings were maintained within ± 1 mV. There was no significant electrode potential deviation within pH range between 2 and 12, which enables the applicability of the electrode in the strong acidic and alkaline products (Fig. 4). The shapes of titration curves and the magnitude of the potential change at the inflection point, at different pH values, additionally confirmed the above statement.

3.3.2. The influence of nonionic surfactants

The nonionic surfactants are very often a component part of anionic surfactants based formulated products. The widely

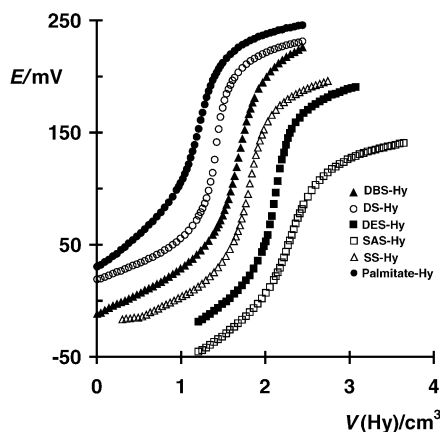


Fig. 3. Titration curves of several commercial anionic surfactants and soap with TA–DS surfactant sensor and Hyamine as titrant (DS = dodecylsulfate; DBS = dodecylbenzensulfonate; DES = dodecylethersulfate; SAS = sec-alkansulfonate; SS = sulfosuccinate).

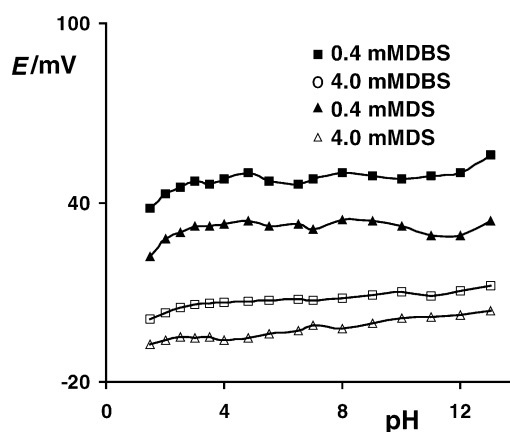


Fig. 4. The influence of pH on the potentiometric response of the TA–DS based surfactant electrode in the solutions of dodecylsulfate (DS) and dodecylbenzensulfonate (DBS).

used class of nonionics are alkoxyated alcohols, which under certain circumstances may exhibit slightly anionic character. Therefore, its influence on the potentiometric titration of anionic surfactants has been investigated. The different amounts of 1% solution of ethoxylated nonylphenol (9EO groups) and

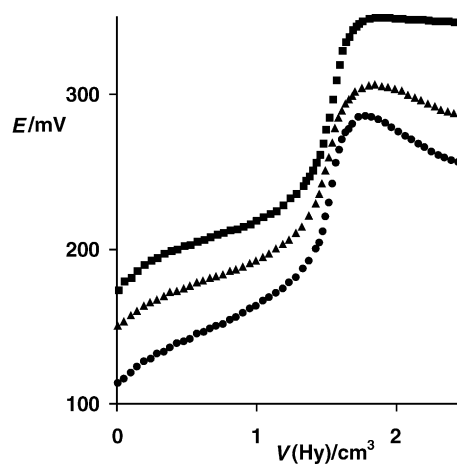


Fig. 5. The influence of nonionic surfactants on the shape of titration curves of DS using Hyamine as titrant and TA–DS surfactant electrode as indicator [(●) 0.5% ethoxylated nonylphenol (9EO groups), (▲) 1.0% ethoxylated nonylphenol (9EO groups), (■) 1.0% ethoxylated undecyl alcohol (3EO)].

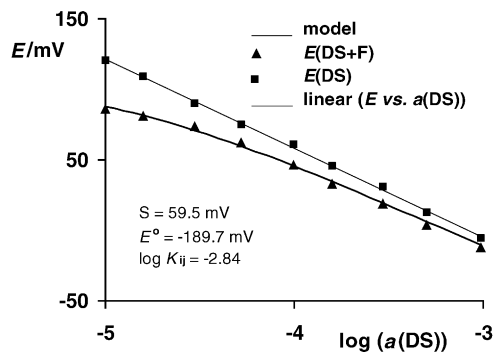


Fig. 6. Estimation of Nikolskii–Eisenman parameters for TA–DS based surfactant electrode by mixed solution method using DS as primary (analyte) ion and fluoride ($c = 0.01 \text{ mol/dm}^3$) as interfering ion.

ethoxylated undecyl alcohol (3EO) were added to the anionic surfactant titrated, and the resulted titration curves are shown in Fig. 5. It can be concluded, that no significant influence on the shape of the titration curves and the magnitude of the potential break has been observed at the specified concentration levels of nonionic surfactants investigated.

3.3.3. Determination of selectivity coefficients

The influence of the interferences on the response of the surfactant electrodes described is defined by the Nikolskii–Eisenman equation:

$$E = E^\circ - \text{slope} \log[a(\text{SAn}^-, \text{det.}) + K^{\text{pot.}}(\text{SAn}^-, \text{det.}; \text{SAn}^-, \text{int.}) \cdot a(\text{SAn}^-)] \quad (6)$$

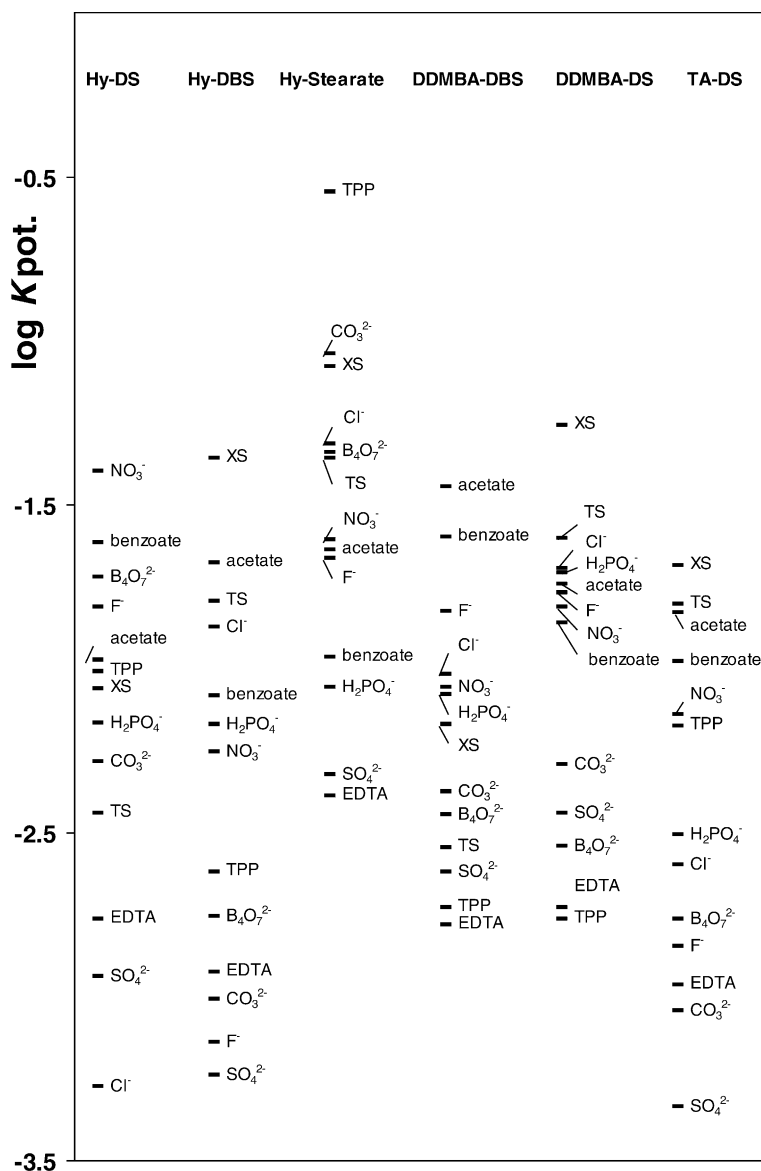


Fig. 7. Selectivity coefficients [$\log K^{\text{pot.}}(\text{SAn}^-, \text{det.}; \text{SAn}^-, \text{int.})$] for different inorganic and organic anions mostly used in commercial formulated products measured with several ion-pair-based surfactant electrodes (XS = xylensulfonate; TS = *p*-toluensulfonate; TPP = tripolyphosphate; EDTA = ethylenediaminetetraacetic acid, disodium salt). Dodecylsulfate was used as the primary (analyte) ion, concentration of the interfering anion ($c = 0.01 \text{ mol/dm}^3$).

where $K^{\text{Pot.}}(\text{SAn}^-, \text{det.}; \text{SAn}^-, \text{int.})$ = selectivity coefficient, $a(\text{SAn}^-, \text{det.})$ and $a(\text{SAn}^-, \text{int.})$ are the activities of analyte, determined ion (det.) and interfering ion (int.), respectively.

The mixed solution method [27] has been used for measurement of selectivity coefficients, which gives more realistic data for the systems investigated, than separate solution method. The electrode response has been measured in a series of solutions of varying primary determined ion activity $a(\text{SAn}^-, \text{det.})$ and fixed interfering ion activity $a(\text{SAn}^-, \text{int.})$. The selectivity coefficients are then estimated graphically, which is very subjective and rough method. The more reliable method is a fitting of Nikolskii–Eisenman equation (used as a model) to the experimental data obtained by mixed solution method [30]. By using solver, an analysis tool incorporated into Microsoft Excel, the minimal sum of squared residuals has been calculated by varying the values of E° , slope and $K^{\text{Pot.}}(\text{SAn}^-, \text{det.}; \text{SAn}^-, \text{int.})$. The calibration graph for dodecylsulfate in the absence and in the presence of interferent (fluoride) ion (F), as well as the model obtained by fitting the experimental data into Nikolskii–Eisenman equation are shown in Fig. 6.

It can be seen, that returned values of the model parameters E° , slope (inserted in Fig. 6) are in good agreement with the electrode response performances (Table 1), taking into account the unknown factors included in the formal electrode potential.

The selectivity coefficients of some potentially interfering, in formulated products usually present inorganic and organic anions, were determined for the TA–DS ion-pair-based electrode, and compared with those of five other ion-pair-based sensors (Fig. 7). By all selectivity measurements dodecylsulfate was used as primary ion in the range of $10 \mu\text{mol}/\text{dm}^3$ and $10 \text{mmol}/\text{dm}^3$, while the concentration of the interfering ion was $10 \text{mmol}/\text{dm}^3$.

The new TA–DS ion-pair-based electrode exhibits a slightly better selectivity performances compared with the other sensors investigated. The most inferior performances, as expected, shows Hy–stearate based sensor. The slightly stronger interferences from *p*-toluensulfonate (TS) and xylensulfonate (XS) do not disturb significantly the potentiometric titration of anionic surfactants, because their concentration in formulated anionic surfactant based products is much lower than that of anionic surfactant used.

4. Conclusions

An all-solid-state surfactant sensitive electrode has been prepared, based on a teflonised graphite conducting substrate coated with plasticised PVC-membrane containing anionic surfactant sensing material. The new synthesized ion-pair-based on a highly lipophylic tetrahexadecylammonium cation and dodecylsulfate as antagonist ion, has been used as surfactant sensor. The electrode exhibited Nernstian response ($58.1 \text{mV}/\text{decade}$) in the region between

$5 \mu\text{mol}/\text{dm}^3$ and $2 \text{mmol}/\text{dm}^3$ for dodecylbenzensulfonate and a near-Nernstian response ($64.2 \text{mV}/\text{decade}$) between $3 \mu\text{mol}/\text{dm}^3$ and $10 \text{mmol}/\text{dm}^3$ for dodecylsulfate. The main application of the electrode described was indication of the end-point in ion-pair surfactant potentiometric titrations. The frequently used anionic surfactants of analytical and technical grade have been successfully titrated and the results compared with those obtained with standard two-phase titration method. The electrode enables the titration of shorter hydrocarbon chain (C_8 , C_{10}) anionic surfactants too, usually, hardly titratable with other methods. The end-point detection of some technical surfactants with slightly higher noise level in the equivalent point region has been improved using multiple point parabola, when calculating the first derivative. The electrode showed satisfactory analytical performances within pH range 2–12. The influence of the widely used class of non-ionic surfactants on the shape of titration curves was negligible. The selectivity performances of the electrode described were superior to those of several other ion-pair-based sensors investigated. The selectivity coefficients were determined by fitting of Nikolskii–Eisenman equation to the experimental data obtained by mixed solution method.

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