

EVALUATION OF EMPIRICAL TITRATION EQUIVALENTS OF CERTAIN TYPES OF INDUSTRIAL SURFACTANTS DETERMINABLE BY POTENTIOMETRIC TITRATION WITH SODIUM TETRAPHENYLBORATE

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Abstract

In this study, it has been shown that potentiometric titration using sodium tetraphenylborate as the titrant can be used as a simple and inexpensive method for the determination of some industrial surfactants commonly used in detergents. Examples of determinations of some cationic and non-ionic surfactants and related calculations are given.

Souhrn

Tato studie ukázala, že potenciometrická titrace používající tetrafenylboritan sodný jako titrant může být použita jako jednoduchá a nenákladná metoda pro stanovení některých průmyslových tenzitů běžně používaných v detergentech. Jsou uvedeny příklady stanovení některých kationtových a neiontových povrchově aktivních látek a související výpočty.

1. Introduction

Surfactants are produced and consumed in large quantities as components of industrial and household detergents. The quantification of surfactants is very important in terms of the evaluation of detergent quality [1].

Many methods have been developed for the determination of surfactants, but most of these methods require sophisticated analytical instruments and specialized personnel [2-5]. Determination of surfactants by using potentiometric titration method is a more practical and inexpensive way. The potentiometric titration method is based on the precipitation of ion pairs formed with a titrant containing the ions at the opposite charge of the surfactant to be determined [6-9]. Due to its anionic character, sodium tetraphenylborate (NaBPh₄) is the most

suitable titrant in potentiometric titrations for the determination of cationic surfactants and nonionic surfactants which can be converted into cationic form [10-12]. The ion pairs resulting from titration with NaBPh₄ have limited solubility in aqueous solutions. The amount of these ion pairs can be measured by means of an indicator electrode having an organic phase in which they can be easily extracted [13]. For this purpose, various types of electrodes may be used which have an organic phase on their sensitive surfaces [14,15].

Besides conventionally fabricated electrodes [16], coated wire electrodes (CWEs) have become more preferred because of their excellent performance, ease of construction and manipulation [17]. In recent years, the use of coated wire electrodes has become even more attractive by reducing the ohmic resistance of the electrodes by mixing carbon powder into the polymeric membrane of these [18].

In this study, examples of titration of certain types of surfactants with NaBPh₄ by using CWE and related empirical titration equivalents are given.

2. Experimental

2.1. Apparatus

The coated-wire electrode (CWE) was prepared as described earlier [6,18] by coating an isolated aluminum wire, with a polymeric membrane from a solution of poly (vinyl chloride) (PVC, 0.09 g) and 2-nitrophenyl octyl ether (NPOE, 0.2 mL) in tetrahydrofuran (THF, 3 mL) and mixed with carbon powder (0.01 g) (Fig. 1).

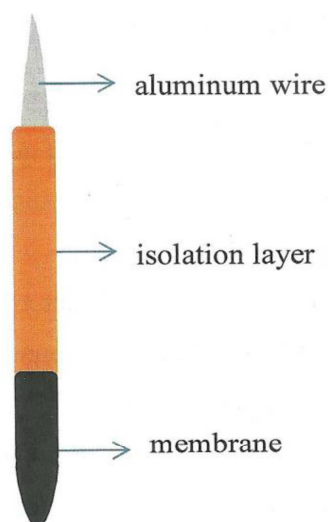


Figure 1. Schematic representation of CWE.

A silver/silver chloride/3.0 M KCl electrode (Metrohm) was used as a reference half-cell and corresponding equilibrium cell voltage measured by using a CPH 52 portable pH meter (Elteca). For titrations, a conventional 10 mL burette was used.

2.2. Solutions and Titration Procedure

In this study, six different cationic and eight different non-ionic industrial surfactants were used to evaluate the empirical titration equivalents. The names, molecular characteristics of surfactants used and the firms in which they were purchased are listed in the table below.

Table 1. List of surfactants investigated in this study

Number	Sample	Commercial or abbreviated name	Molecular weight g mol ⁻¹	Firm
Cationic surfactants				
I	Hexadecylpyridinium chloride monohydrate	CPC	358	Sigma (Steinheim-Germany)
II	Didecyldimethylammonium chloride	Arquad 2.10-50	362	AkzoNobel (Stenungsund-Sweden)
III	1,3-Didecyl-2-methylimidazolium chloride	Tegotrants A100	399	Sigma-Aldrich (Steinheim-Germany)
IV	Benzethonium chloride	Hyamine	448	Sigma (Steinheim-Germany)
V	Cetyl-trimethyl-ammonium bromide	CTAB	364	Janssen Chimica (Beerse-Belgium)
VI	Didodecyldimethylammonium bromide	DDDMAB	462	Sigma-Aldrich (St. Lois-USA)
Polyethyleneglycol and nonionic surfactants				
				Number of OEUs*
VII	Polyethyleneglycol 600	PEG-600	13.2	Sigma-Aldrich (Steinheim-Germany)
VIII	4-(1,1,3,3-Tetramethylbutyl) phenyl-polyethylene glycol	Triton X-100	9.5	Sigma-Aldrich (Steinheim-Germany)
IX	Glycereth-17 Cocoate	Levenol C-201	17	Kao Corporation (Barcelona-Spain)
X	Glycereth-7 Cocoate	Levenol C-301	7	Kao Corporation (Barcelona-Spain)
XI	Glycereth-2 Cocoate	Levenol C-421	2	Kao Corporation (Barcelona-Spain)
XII	Glycereth-6 Cocoate	Levenol F-200	6	Kao Corporation (Barcelona-Spain)
XIII	-	Berol-185	11	AkzoNobel (Stenungsund-Sweden)
XIV	-	Berol Surf-boost AD15	?	AkzoNobel (Stenungsund-Sweden)

* In Table 1, OEUs means oxyethylene units.

Analyte solutions of cationic surfactants were prepared by diluting 5 mL portions of 0.01 M stock solutions of these surfactants to 50 mL. The stock solutions of the non-ionic surfactants were prepared to be about 0.5 g / 100 mL of water from the corresponding surfactant. 15 mL of barium(II) chloride solution (BaCl_2 , 0.1 M) and 30 mL of distilled water were added to 2 mL portions of these solutions to obtain the analyte solutions used in titrations.

NaBPh_4 titrant solution (0.00984 M) was prepared by dissolving the substance in deionized water, adjusting pH to 9 with sodium hydroxide and diluting with water to the required volume. The NaBPh_4 solution was standardized against 0.01008 M thallium(I) nitrate solution [8].

Titration consumption from the first derivatives of the titration curves was used to calculate the empirical titration equivalents. Excel graphical program was used to obtain these first derivative curves and to evaluate corresponding end-points.

3. Results and Discussion

As mentioned in the introduction, titrimetric procedures for the ionic surfactants to be determined generally depend on the precipitation of ion pairs [6,7]. The end points of these titrations can be observed with the help of a suitable indicator electrode. In the determination of cationic surfactants, the use of NaBPh_4 as a titrant of the anionic character is very suitable for the formation of the corresponding ion pairs [10].

As a result of the NaBPh_4 titrations of the cationic surfactants used in this study (Fig. 2.), the curves were obtained that have sharp potential breaks which allowed the determination of the end points and thus, empirical titration equivalents could be calculated.

The titrimetric determination of nonionic surfactants has some differences compared to those of cationic surfactants. Nonionic surfactants as the compounds containing poly (oxyethylene) chains need to be converted to positive charged forms precipitating with NaBPh_4 [11,12]. This conversion can be accomplished by adding an excess of a divalent metal ion such as barium (Ba^{2+}) to the analyte solution. Previous studies have shown that an average of 5.2 oxyethylene units (OEUs) correspond to a tetrafenylborate ion, i.e., 10.4 units of each Ba^{2+} ion [12]. For this reason, titrations were carried out by adding BaCl_2 solutions to the analyte solutions of the nonionic surfactants as mentioned in the experimental part. Related titration curves are shown in Fig. 3.

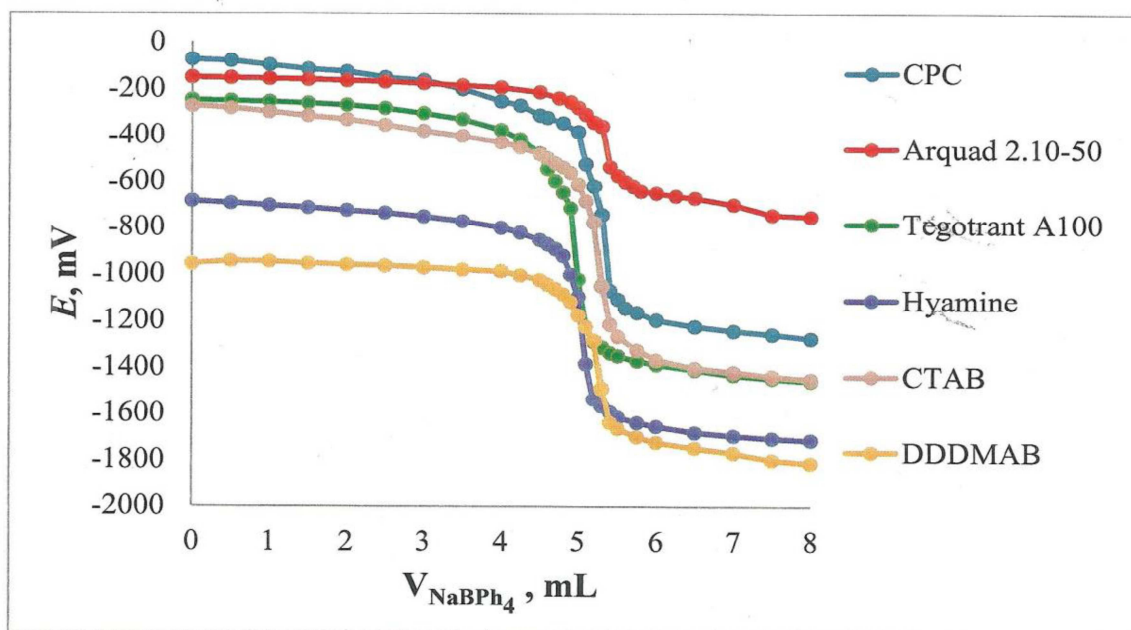


Figure 2. Titrations of cationic surfactants used in this study with NaBPh₄ by using CWE.

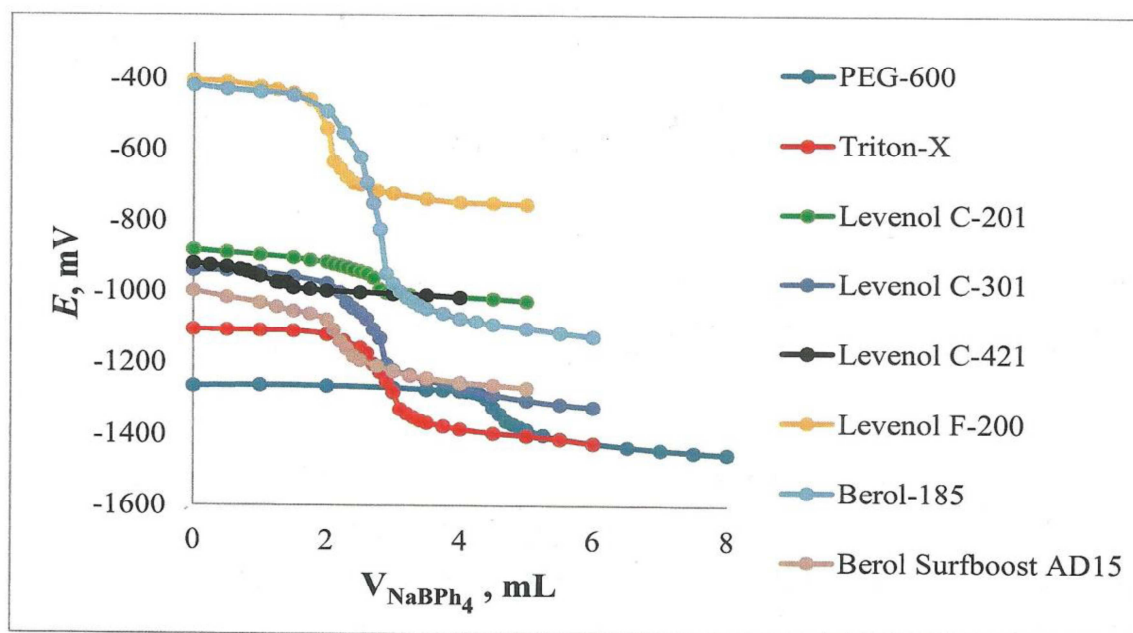


Figure 3. Titrations of non-ionic surfactants used in this study with NaBPh₄ by using CWE.

It is said in the literature that nonionic surfactants which can be determined by NaBPh₄ titration should contain at least 5 OEUs [12]. All nonionic surfactants examined in this study included 6 or more OEUs, except one (XI: Levenol C-421). Indeed, titration of the

same volume of the surfactant XI analyte solution could not be performed. In order to overcome this, it was necessary to increase the analyte volume 10-fold (20 mL). Only in this way a titration curve with a potential jump of 21 mV could be obtained to allow calculation of the titration equivalent.

The empirical titration equivalents calculated from the NaBPh₄ titrations of the surfactants used in the study are given in Table 2.

Table 2. Results of empirical equivalents obtained from the NaBPh₄ titrations of some cationic and nonionic surfactants

Sample	Amount of sample mg	NaBPh ₄ consumption mmol	Empirical equivalent mg mmol ⁻¹
I	17.90	0.05263	340
II	18.23	0.05260	347
III	19.96	0.04869	410
IV	22.44	0.05017	447
V	18.34	0.05164	355
VI	23.09	0.05164	447
VII	10.03	0.04378	229
VIII	10.22	0.03000	341
IX	10.19	0.02705	377
X	10.02	0.02804	357
XI	101.16	0.01722	5875
XII	10.10	0.02017	501
XIII	9.99	0.02804	356
XIV	10.04	0.02115	475

4. Conclusions

The results obtained from this study have shown that empirical titration equivalents can be used successfully for the determination of some cationic and nonionic type of surfactants. The proposed method is considerably inexpensive, practically compared to other methods used in this field, and does not require any special expertise. For the aforementioned reasons, it can be said that the proposed method can be used safely in analytical laboratories of the detergent industry.

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