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**CARBON PASTE ION-SELECTIVE ELECTRODE
FOR ION-PAIR FORMATION-BASED
POTENTIOMETRIC TITRATIONS OF ANIONIC
SURFACTANTS**

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In this contribution, a new carbon paste ion-selective electrode was introduced for ion-pair formation-based potentiometric titrations of anionic surfactants. In the electrode, an extract of hexadecylpyridinium dodecylsulfate in o-nitrophenyl octyl ether was used as both the binder and the electroactive ion-exchanger. Concerning titrants, three cationic compounds were examined: hexadecylpyridinium chloride (CPC), (diisobutylphenoxyethoxyethyl)-dimethyl-benzyl-ammonium chloride (Hyamine 1622, HYA) and 1,3-didecyl-2-methylimid-azolium chloride (Tegotrant A100, TGT). The last one gave potentiometric titration curves with the highest potential breaks (210–260 mV), followed with CPC (90–140 mV) and HYA (40–60 mV). Despite this, the practical use of TGT in control laboratories should economically be considered impossible for its too high price on market. According to the authors' meaning, the use of CPC as a titrant seems

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to be the best compromise as the steepness of the corresponding titration breaks is sufficient and its price is acceptable as well.

Introduction

Titrimetric determinations of inionic surfactants are usually based on the formation of ion-pairs between the determinand (which contains either lipophilic anion or lipophilic cation) and the titrant containing an oppositely charged lipophilic ion. Thus, these “antagonistic” titrations involve precipitation of an ion-pair of limited solubility in aqueous media, i.e.,



As early as in 1945, Jones [1] noted in his work with Methylene Blue that cationics interfere with the solvent solubility of the cationic dye-anionic surfactant associate. The next development was the procedure of Epton [2,3], who suggested to titrate one ionic type of surfactant with the opposite type in the presence of the abovementioned dye as the indicator in the presence of an other solvent. The transfer of the indicator colour ion-pair form from one phase to the other (the dye transfer) is taken as the titration end-point. The method was continually developed. Thus, for example, Cahn [4] observed the transfer of dichlorofluorescein during a titration of cationics with an anionic surfactant in the presence of a chlorinated solvent, Barr [5] introduced the use of Bromophenol Blue. Generally, there are the phenomena utilized by the dye transfer method [6]:

- (i) The solvent-soluble associate of an anionic surfactant with a basic dye is destroyed by a cationic surfactant, and the dye released into the aqueous phase;
- (ii) The solvent-soluble salt of a cationic surfactant with an acid dye is destroyed by an anionic surfactant and the dye released into aqueous phase;
- (iii) The water-soluble mixture of an anionic surfactant and an acid dye yields the dye to excess cationic surfactants, forming solvent-soluble ion-pairs;
- (iv) The water-soluble mixture of a cationic surfactant and a basic dye yields the dye to excess anionic surfactants, forming solvent-soluble ion-pairs.

Therefore, regardless of what is titrated with what (and independently of the dye used), the equivalence point of equal moles of both types of surfactants just precedes the transfer of the dye from one phase to another. Over last 60 years, numerous papers have been published describing improvements, modifications and special applications of these so-called “two phase” or “Epton titrations”. One of the variants [7] was developed at the behest of the Commission Internationale d’Analyses and later, a critical review was published [8]. The method has become

the international standard method described in ISO 2271, ISO 2871-1 and ISO 2871-2, all of them are almost identical. In the method, chloroform as the organic phase and a mixed indicator containing Disulphine Blue VN and dimidium bromide are recommended (for details, see Ref. [9]).

Possibilities for end-point indication have been extended simultaneously with the development of ion-selective membrane electrodes in the seventies of the last century, a period called also “the gold age” of these potentiometric sensors. Gavach *et al.* were probably the first applying such electrodes in potentiometric titrations of both cationic [10] and anionic [11] surfactants. Later, several other papers dealt with applications of ion-selective electrodes in titrimetric analysis of ionic surfactants (for some detailed literature references, see Refs [12] and [13]). The main advantages of potentiometric as opposed to two-phase titrations are [9]:

- (i) It permits the use of much higher concentrations of titrants, resulting in sharper end-points and thus better reproducibility;
- (ii) It is less subjective;
- (iii) It eliminates the use of chloroform, whose vapor is toxic and may be carcinogenic;
- (iv) It readily lends itself to automation;
- (v) It is much less fatiguing for the operator.

In addition to the facts mentioned above, it was reported [14] that the indicator recommended for the two-phase titration of surfactants is probably mutagenic. Till this time, procedures involving potentiometry and potentiometric titrations have been described which allow reliable determination of surfactants of various types [9,15,16]: anionic, cationic, ampholytic, as well as non-ionic. As supported by recent investigations [17-22], this method represents an ecological alternative to the official titration procedure.

Concerning surfactant-selective electrodes, they are usually based on a liquid/plastic membrane which is incorporated to the electrode body and which separates two aqueous media, thus representing a three-phase system

internal electrolyte | membrane | external electrolyte (sample solution)

In early designs, the organic phase of such membranes was an organic solvent, placed between the two aqueous phases in a bulk or with the support of a thin, porous cellulose sheet, sintered glass, or the like. As work with these membranes proceeded, more durable polymer supports were developed, most often polyvinyl chloride (PVC), which is now used almost universally for this type of electrodes. An electroactive compound (an ion-pair in which ionic surfactants participates) is dissolved in a solvent (usually tetrahydrofuran or cyclohexanone) together with the PVC and a suitable plasticizer. The solvent evaporates, leaving a plasticized PVC surfactant-selective membrane. Because the plasticized polymer

membrane behaves like a viscous liquid, the properties of the electrode are very similar to those of the original wet membrane. It should be noted that virtually any ionic species can be detected and measured by such liquid ion-exchange electrodes. To built a membrane responsive to anion X^- , for example, the Q^+X^- ion-pair is dissolved in a nonvolatile solvent; the Q^+ cation must be highly lipophilic. Similarly, for an electrode responsive to cation Q^+ , an oil-soluble salt is used, where the X^- anion is lipophilic. These rules are observed in the construction of various electrodes, including also some organic ion-selective sensors [23-25]. In the following papers, one could follow more and more applications of commercial surfactant-sensitive electrodes; a specialized monograph describing their use was also edited [26].

At the same time, it was found that carbon paste electrodes (CPEs) can serve as potentiometric indicators to monitor the titrations of surfactants as well [27]. Their use is advantageous namely for their very low ohmic resistance (less than $10\ \Omega$ instead of up to $M\Omega$ values for electrodes based on polymeric membranes). The idea of an application was realized when some new types of carbon pastes were obtained by mixing a carbon powder with the same liquids used as plasticizers in potentiometric plastic membrane electrodes [28,29]. As reported very recently, the optimum ratio of carbon powder to pasting liquid contents in corresponding pastes can be experimentally found by simple measurements of their ohmic resistance [30,31]. This paper presents a new type of the carbon paste-based surfactant ion-selective electrode and its application to monitor potentiometric titrations using three cationic titrants.

Experimental

Chemicals and Instrumentation

As titrants, 0.01 M solutions of three cationic compounds were tested: hexadecylpyridinium chloride (CPC), 1,3-didecyl-2-methylimidazolium chloride (Tegotrant A100; further TGT), and also (diisobutylphenoxyethoxyethyl)-dimethylbenzylammonium chloride (Hyamine 1622; HYA). For the preparation of the ion-exchanger, 0.01 M sodium dodecylsulfate (SDS) solution was also used. All the chemicals were of analytical-reagent grade and purchased from Sigma-Aldrich. Model samples of liquid detergents containing anionic surfactants were obtained from Tomil, Vysoké Mýto. Deionized water was used throughout.

The potentiometric cell used comprised the indicator carbon paste electrode (CPE) and reference $\text{Ag}|\text{AgCl}|3\text{M KCl}$ electrode. The cell voltage was measured by means of the portable pH meter, model CPH 52 (Elteca, Turnov). For dosing the titrants, a conventional 10-ml burette was used.

Preparation of Carbon Paste Surfactant Ion-Selective Electrode

A sensing electrode was prepared by thorough mixing of 1.0 g graphite powder (CR-5, Maziva, Týn nad Vltavou) and 0.4 ml pasting liquid, which was an *o*-nitrophenyloctyl ether extract of hexadecylpyridinium dodecylsulfate (roughly equal volumes of CPC and SDS solutions of the same concentrations were mixed and the precipitated form was extracted using a small volume of the organic liquid). Then, the paste was packed into a piston-like electrode body with a conductive contact. During measurements, the paste active surface was renewed by polishing on filter paper. When stored, the electrode was immersed in water at room temperature.

Results and Discussion

During a preliminary test, a model sample was titrated using CPC with the assay of 75.7 % which agreed quite well with the declared content (about 75 %). Thus, the next attention was paid to the comparison of potentiometric titration curves taken with the use of other titrants. The results indicated, that the height of the potential break near the end-point decreased in order

TGT (210-260 mV) > CPC (90-140 mV) > HYA (40-60 mV).

Shapes of potentiometric titration curves are documented in Fig. 1. It should

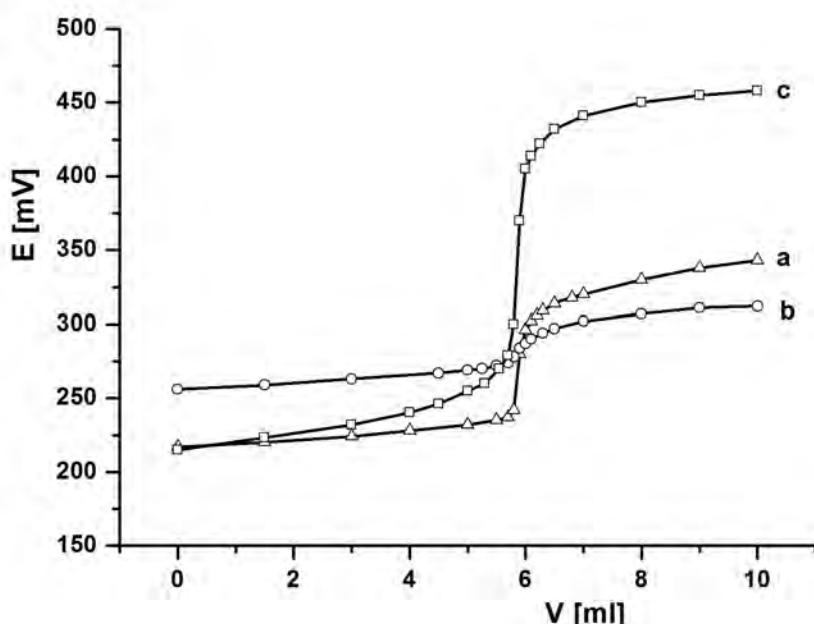


Fig. 1 Comparison of potentiometric titration curves of sample containing anionic surfactant (SDS) titrated using 0.01 M solutions of CPC (a), HYA (b), and TGT (c)

be mentioned that in agreement with the first preliminary determination mentioned above, we obtained results (in the same order of titrants) of 75.8 %, 75.7 %, and 76.0 %. However, it was also found that the HYA titrant, frequently applied for industrial control laboratories using methods of two-phase titrations, cannot be recommended for potentiometric titrations indicated with this kind of the electrode. First, corresponding potential break is small and, in addition, its steepness is not favourable either. Thus, in further studies, the use of HYA was eliminated.

The method was further verified on four model mixtures of detergents containing varied amounts of anionic surfactants in various liquid matrices (for example, a rinsing waste water was represented by sample No. 4). The results (averages of three parallel measurements) are listed in Table I. Evidently, no accuracy test could be applied because of the approximative character of the contents declared. However, both precision and mutual agreement of results obtained with the two titrants could be evaluated applying a simple Lord's *u*-test [32]. As can be seen, none of the *u* values calculated is higher than the critical one.

Taking into account our observations, the TGT titrant seems to be the best as regards the height of corresponding potential end-point breaks. However, its use in control laboratories is disputable from the economic point of view (marketed for ca. 600 CZK per 1 g substance). Concerning CPC, its price is substantially more acceptable (ca. 1000 CZK per 100 g)! In addition to that, potential breaks using CPC are not so high but steep enough and thus, the end-points of the titration curves can reliably be evaluated.

Table I Analyses of model detergent samples titrated using either TGT or CPC

Sample No.	Content, %		Titrant	Lord's test ^b
	Declared	Found ^a		
1	~60	57.2 ± 1.1	TGT	0.091
		57.4 ± 1.1	CPC	
2	~20	22.3 ± 0.8	TGT	0.118
		22.5 ± 0.9	CPC	
3	~27	28.9 ± 1.9	TGT	0.552
		27.3 ± 1.0	CPC	
4	~3	3.07 ± 0.90	TGT	0.037
		3.14 ± 1.00	CPC	

^a) Given as $x \pm R$, where x is the arithmetic mean, R the range.

^b) Lord's *u* values calculated for three replicates of each determination; its critical value for the significance level $\alpha = 0.05$ is $u_{\text{crit}} = 0.636$.

Conclusion

In this contribution, recently developed method for determination anionic surfactants in detergent mixtures is presented. The method is based on the potentiometric titration when employing the ion-pair formation and the use of carbon paste ion-selective electrode. Within this study, hexadecylpyridinium chloride (CPC), (diisobutylphenoxyethoxyethyl)dimethylbenzylammonium chloride (HYA) and 1,3-didecyl-2-methylimidazolium chloride (TGT) were tested as titrants. The best results were obtained with TGT, but when taking into account its price, the more reasonable seems to be the second titrant, which is CPC. Even if it seems that more sophisticated instrumental techniques have replaced older potentiometric titrations, this contribution reflects the reality in some commercial laboratories where the suggested method still represents an effective application.

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References

- [1] Jones J.H.: J. Assoc. Offic. Agr. Chemists **28**, 398 (1945).
- [2] Epton S.R.: Nature **160**, 795 (1947).
- [3] Epton S.R.: Trans Faraday Soc. **44**, 226 (1948).
- [4] Cahn F.: U. S. Pat. 2,471,861; Chem. Abstr. **43**, 6948h (1949).
- [5] Barr T., Oliver J., Stubbings W.V.: J. Soc. Chem. Ind. (London) **67**, 45 (1948).
- [6] Rosen M.J., Goldsmith H. A.: *Systematic Analysis of Surface-Active Agents*, 2nd ed., p. 421. Wiley-Interscience, New York, 1972.
- [7] Reid V.W., Longman G. E., Heinerthe E.: Tenside **4**, 292 (1967).
- [8] Reid V.W., Longman G. E., Heinerthe E.: Tenside **5**, 90 (1968).
- [9] Cullum D.C. (Ed.): *Introduction to Surfactant Analysis*, Chapman & Hall, London, 1994.
- [10] Gavach C., Seta F.: Anal. Chim. Acta **50**, 407 (1970).
- [11] Gavach C., Bertrand C.: Anal. Chim. Acta **55**, 385 (1971).
- [12] Vytrás K., Dajková M., Mach V.: Anal. Chim. Acta **127**, 165 (1981).
- [13] Vytrás K.: Ion-Sel. Electrode Rev. **7**, 77 (1985).
- [14] Buschmann N.: J. Am. Oil Chem. Soc. **72**, 1243 (1995).
- [15] Vytrás K.: Electroanalysis **3**, 343 (1991).

- [16] Vytřas K.: Egypt. J. Anal. Chem. **5**, 107 (1997).
- [17] Schmitt T.M.: *Analysis of Surfactants*, 2nd ed., p. 490. Marcel Dekker, New York, 2001.
- [18] Buschmann N., Schultz R.: Jorn. Com. Esp. Deterg. **23**, 323 (1992).
- [19] Sanchez J., del Valle M.: Crit. Rev. Anal. Chem. **35**, 15 (2005).
- [20] Madunić-Čačić D., Sak-Bosnar M., Matešić-Puač R.: Int. J. Electrochem. Sci. **6**, 240 (2011).
- [21] Wang J.W., Du Z.P., Wang W.X., Xue W.: Turk. J. Chem. **36**, 545 (2012).
- [22] Madunić-Čačić D., Sak-Bosnar M., Matešić-Puač R., Samardžić M.: Int. J. Electrochem. Sci. **7**, 857 (2012).
- [23] Vytřas K.: J. Pharm. Biomed. Anal. **7**, 789 (1989).
- [24] Vytřas K.: *Contemporary Trends in the Use of Ion-Selective Electrodes in the Analysis of Organic Substances*, in Churáček J. (Ed.): *Advanced Instrumental Methods of Chemical Analysis*, p. 142. Academia, Prague, and Horwood, Chichester, 1993.
- [25] Vytřas K.: *Potentiometry*, in Swarbrick J., Boylan J.C. (Eds): *Encyclopedia of Pharmaceutical Technology*, Vol. 12, p. 347. Marcel Dekker, New York, 1995.
- [26] Schulz R.: *Determination of Ionic Surfactants in Cosmetic Products* (in German). Metrohm, Herisau, 1995.
- [27] Vytřas K., Ježková J., Kalous J., Švancara I. in: *XXVIII. seminář o tenzidech a detergentech* (in Czech), p. 35. Sloveca, Nováky, 1994.
- [28] Švancara I., Vytřas K.: Anal. Chim. Acta **273**, 195 (1993).
- [29] Ježková J., Musilová J., Vytřas K.: Electroanalysis **9**, 1433 (1997).
- [30] Mikysek T., Švancara I., Kalcher K., Bartoš M., Vytřas K., Ludvík J.: Anal. Chem. **81**, 6327 (2009).
- [31] Mikysek T., Stočes M., Švancara I., Vytřas K.: Chem. Listy **108**, 513 (2014).
- [32] Lord E.: Biometrika **34**, 41 (1947).