Int. J. Electrochem. Sci., 6 **(2011)** 1630 - 1641

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Investigation of Homologous Tallow Fatty Alcohols and Oleyl Alcohol Ethoxylates Using a Potentiometric Surfactant Sensor

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Received: 5 April 2011 / *Accepted:* 26 April 2011 / *Published:* 1 May 2011

The homologous tallow fatty alcohol and oleyl alcohol ethoxylates were investigated using a PVC liquid surfactant sensor based on 1,3-didecyl-2-methylimidazolium-tetraphenylborate as a sensing element and bis(2-ethylhexyl) phthalate as a plasticizer. The sensor responded to the tetraphenylborate (TPB) ion according to the Nernst equation (slope = -59.1 mV/decade of activity) in the region of 5×10^{-6} to 1×10^{-2} M, and it reached 95 % of its equilibrium response for the TPB ion within 10 s for the concentration change of 1×10^{-6} M→1×10^{-5} M, and in 5 s for the concentration change of 1×10^{-5} M → 1×10^{-3} M. The sensor was successfully used for the potentiometric titration of the homologous tallow fatty alcohol and oleyl alcohol ethoxylates. The accuracy of the determination was 98.6 % - 100.8 % for both alcohol ethoxylates investigated. The reaction stoichiometry of the potentiometric titration of ethoxylated nonionic surfactants (EONS) investigated was also studied.

Keywords: Surfactant sensor, nonionic surfactant, ethoxylated, tallow fatty alcohol, oleyl alcohol, potentiometric titration

1. INTRODUCTION

Nonionic surfactants are surface-active compounds that are non-ionizable in aqueous solutions that consist of a lipophilic part (e.g., alkylated phenols, fatty acids, long-chain linear alcohols) and a hydrophilic part (primarily ethylene oxide chains of various lengths). These compounds are second in worldwide surfactant consumption, comprising 35 % of the total surfactant market.

The most interesting, commercially-available nonionic surfactants are ethoxylated nonionic surfactants (EONS). This paper focuses on ethoxylates of tallow fatty alcohol (C_{16}-C_{18}) and oleyl alcohol, which are both widely used in detergents, household cleaning and personal care products.

EONS can be used to build analytically important complexes with numerous monovalent and divalent cations of alkali, earth alkaline and transition metals [1-3]. Complexes of EONS with barium ions have been exploited for the potentiometric determination of EONS, based on the reaction of pseudocationic complexes of EONS and barium with tetraphenylborate (TPB).

The potentiometric titration of polyoxyethylenes was presented for the first time by Levins and Ikeda [4]. They investigated the precipitation of polyethylene glycols in the presence of barium ions using sodium tetraphenylborate (NaTPB) as a titrant; they reported that barium ions react stoichiometrically with tetraphenylborate (TPB), forming a complex precipitate containing barium ions and TPB in a 1:2 ratio. NaTPB is generally accepted as a titrant in potentiometric titrations of polyoxyethylenes.

TPB salts of pseudocationic complexes of EONS with barium [5-12] and lead [13-14] are typically used for polyoxyethylene chain complexation; in addition, they have been used as a sensing material in different types of potentiometric, primarily liquid membrane EONS sensitive electrodes. They are extensively used in the investigation of critical micelle concentration (CMC) values [6-8, 11,15] for EONS and for studies on the stoichiometry composition of ternary metal complexes formed [12, 16-19].

In this paper, a poly(vinyl chloride) (PVC) liquid membrane surfactant-sensitive electrode containing 1,3-didecyl-2-methylimidazolium-tetraphenylborate (DMI-TPB) as an electroactive recognition element was employed for the characterization and potentiometric titration of the tallow fatty alcohol and oleyl alcohol ethoxylates.

2. EXPERIMENTAL

2.1. Reagents and materials

All reagents used were of high purity or analytical grade, except the technical grade surfactants. The solutions were prepared with deionized water (18.2 MΩ cm specific resistance) .

The following EONS were used:

Analytical grade EONS: Triton X-100 (Merck, Germany) and Brij 35 (Sigma-Aldrich, Switzerland).

Technical grade EONS: Genapol O 080, Genapol O 100, Genapol O 120, Genapol O 200, Genapol T 080, Genapol T 110, Genapol T 150, Genapol T 200, Genapol T 250, Genapol T 500 and Genapol T 800 [all obtained from Clariant (Germany) with declared purity higher than 99 % and used without further purification].

The chemical names, mean M_r and mean number of EO groups for all the surfactants are given in Table 2.

A sodium tetraphenylborate (Fluka, Switzerland) solution (c = 5 mmol/L), buffered with borate buffer solution at pH 10.0, was used as titrant. A barium chloride (Fluka, Switzerland) solution [c = 0.2 mol/L, acidified with conc. HCl (1 mL/L)] was used for the pseudo-ionic complex formation.

The self-made ion-exchange complex, high molecular weight poly(vinyl chloride), bis(2-ethylhexyl) phthalate (DEHP) as a plasticizer and tetrahydrofuran as a solvent were used for the preparation of the surfactant sensitive membrane. All reagents used for the membrane preparation were Selectophore ® grade (Fluka, Switzerland).

2.2. Preparing of the PVC membrane electrode

2.2.1. Electrode membrane preparation

The 1,3-didecyl-2-methylimidazolium-tetraphenylborate (DMI-TPB) was used as the electroactive material in the PVC liquid membrane and successfully employed in the potentiometric titrations of ionic surfactants (DMI-TPB electrode**)** [20,21]. DMI-TPB was prepared by the addition of a sodium tetraphenylborate solution to a 1,3-didecyl-2- methylimidazolium chloride solution. The white precipitate was extracted with dichloromethane and dried with anhydrous sodium sulfate. After evaporation and recrystallization from the mixture of diethylether: methanol (1:1), the isolated white DMI-TPB crystals were used for the membrane preparation. The detailed preparation of the sensing material was described previously [20].

The membrane was prepared from bis(2-ethylhexyl) phthalate (DEHP) as plasticizer, high molecular weight PVC and the DMI-TPB complex as the sensing material (1 wt %). The plasticizer: PVC ratio was 3:2. The membrane components (total 180 mg) were dissolved in 2 mL tetrahydrofuran. The clear solution was poured into a glass ring (i.d. 24 mm) fixed on a glass plate, and after curing, small disks (i.d. 7 mm) were punched from the cast film.

The chemical structure of electroactive membrane material and plasticizer used for membrane preparation are shown in Figure 1.

2.2.2. Electrode preparation and maintenance

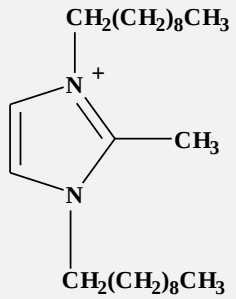
The membrane was mounted on a Philips electrode body IS-561 (Glasblaeserei Moeller, Zurich, Switzerland). A sodium chloride solution (c = 1 mol/L) was employed as the internal filling solution (DMI-TPB DEHP electrode).

After performing the titrations, the membrane was regularly controlled and cleaned because the precipitate was inclined to adhere to the membrane surface. To clean the surface, the surface should be rinsed in a large volume of water with high speed mixing on the magnetic stirrer. From time to time, the membrane should be cleaned with a soft cloth dampened with methanol : water (1:1) and rinsed as described. Between measurements, the electrode was kept either in deionised water or dry.

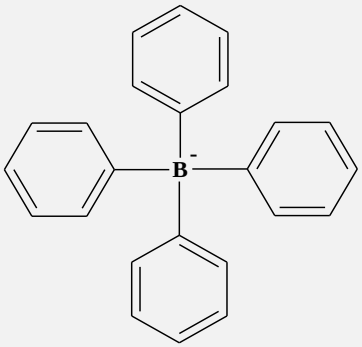
A silver/silver (I) chloride reference electrode (Metrohm, Switzerland) with a reference electrolyte sodium chloride solution (c = 1 mol/L) was used as one reference. The lifetime of the electrode was several months.

Electroactive membrane material

1,3-didecyl-2-methyl imidazolium (cation)

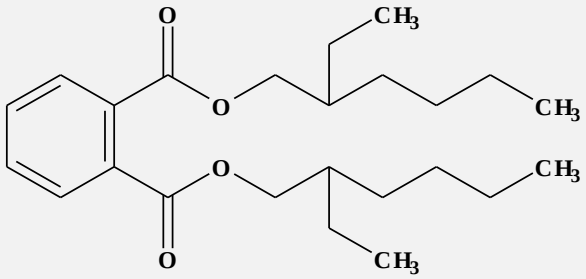


Tetraphenylborate (anion)



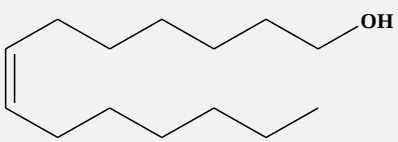
Plasticizer

Bis(2-ethylhexyl) phthalate (DEHP)

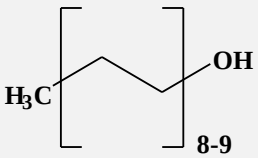


Lipophilic part of nonionic surfactant molecules investigated

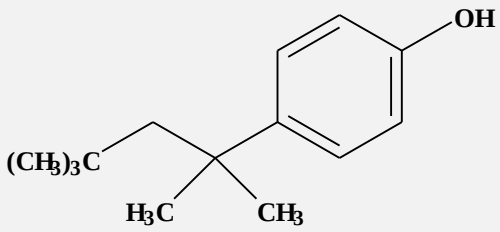
Genapol O series: **Oleyl alcohol**



Genapol T series: **Tallow fatty alcohol**



Triton X-100



Brij 35

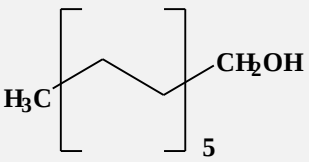


Figure 1. Chemical structures of electroactive membrane material, the plasticizer used for membrane preparing and lipophilic part of the nonionic surfactant molecules investigated.

2.3. Apparatus

A model 808 Titrando (Metrohm, Switzerland) combined with Metrohm 806 exchange units was used to perform all characterizations and potentiometric titrations. During the titrations, the solutions were magnetically stirred using the Metrohm stirrer, model 727 Ti stand.

2.4. Procedure

2.4.1. Dynamic response measurement

The dynamic response of the electrode was measured by applying the activity step method, according to the IUPAC definitions [22], by successive injection of the concentrated solutions of TPB into a magnetically stirred solution.

2.4.2. Titrations

In all titrations, the amount of EONS was 5 mg. The barium chloride solution (V = 5 mL, c = 0.2 mol/L) was added to the solution before titration. The total volume of the solution used for the titration was 50 mL. All measurements and titrations were performed at room temperature using a magnetic stirrer, without ionic strength or pH adjustment.

The titrator was programmed to work in DET (Dynamic Equivalent point Titration) mode with dosing increments of 0.01 to 0.2 mL, a signal drift of 5 mV/min and the equilibrium time between 20 and 60 s. The wait time before the start of the titration varied between 60 and 120 s, depending on the sensitivity of the electrode toward the surfactant investigated or when the electrode reached a stable value in the titrated solution.

3. RESULTS AND DISCUSSION

3.1. Effect of plasticizer type

The influence of the plasticizer on the sensor performance was studied using two membrane plasticizers: DEHP and *o*-nitrophenyloctylether (*o*-NPOE). Thus, Triton X-100 was potentiometrically titrated using the DMI-TPB sensor containing each of the plasticizers separately and using STPB as the titrant.

At the beginning, the membrane plasticized with o-NPOE exhibited a higher potential jump at the end point area; during the procedure, a loss of precision and reproducibility was observed, resulting in a short lifetime of the sensor.

Although the membrane containing DEHP revealed a slightly lower potential jump at the inflexion and a slower dynamic response, this membrane was chosen for further investigations due to the higher reproducibility and membrane stability (longer lifetime).

3.2. Response characteristics

3.2.1. Response toward tetraphenylborate

Standard sodium TPB was used as a titrant for the potentiometric titration of Ba-EONS pseudocationic complex. In addition, TPB was a component of the ion-exchange complex that was used as the sensing material in the electrode membrane.

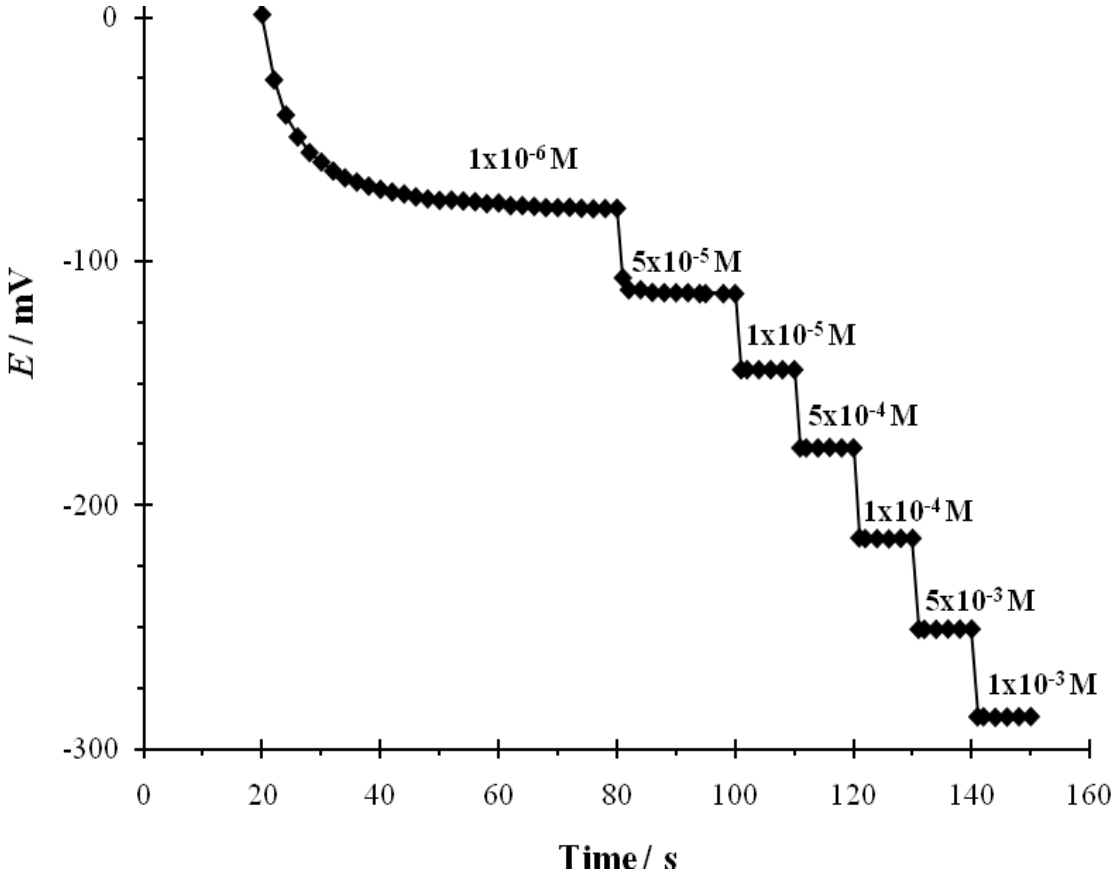


Figure 2. Dynamic response characteristics of the DMI-TPB surfactant sensor in TPB solutions (at stepwise changes of TPB concentration).

Thus, the investigation of the sensor response toward TPB was of great importance for the shape and magnitude of titration curve inflexion and the sensitivity of the titration procedure.

The sensor responded to the TPB ion according to the Nernst equation as follows:

$$E = E^0_{TPB^-} + S_{TPB^-} \times \log a_{TPB^-} \quad (1)$$

A strong correlation was observed between the electromotive force (EMF) measured (E) and the logarithm of the TPB activity in the region of 5×10^{-6} to 1×10^{-2} M. The electrode exhibited an

almost theoretical response toward TPB (slope = -59.1 mV/decade of activity), according to Equation (1). The activity coefficients for TPB were calculated according to the Davies equation.

The dynamic response of the DMI-TPB surfactant sensor was also evaluated.

As shown in Figure 1, the sensor reached 95 % of its equilibrium response for the TPB ion within 10 s for the concentration change from 1×10^{-6} M→1×10^{-5} M and in 5 s for the concentration change of 1×10^{-5} M→1×10^{-3} M.

3.3. Interferences

EONSs are known to form complexes with alkali and alkaline earth metals [16]. Some complexes reveal a pseudocationic character and are readily precipitated with TPB. Small inorganic cations (e.g., Li^+, Na^+) interfered slightly, whereas potassium interfered strongly due to its precipitation reaction with TPB. Barium and lead seriously interfered. The sensor can be used in the pH range of 3 to 11.

3.4. Potentiometric titration

The potentiometric determination of EONS was based on the titration of pseudocationic barium complexes of EONS with sodium tetraphenylborate as titrant.

Barium ion forms pseudocationic complexes with EONS as follows:

$$Ba^{2+} + xEONS \rightleftharpoons \left[Ba\left(EONS\right)_x\right]^{2+} \qquad (2),$$

or simplified as the following:

$$Ba^{2+} + xL \rightleftharpoons BaL_x^{2+} \qquad (3),$$

where $L = EONS$.

The "*x*" value depends on the number of ethoxy (EO) units in the surfactant molecule.

The formed complex can be titrated with sodium tetraphenylborate as follows:

$$BaL_x^{2+} + 2TPB^- \rightleftharpoons BaL_x\left(TPB\right)_2 \qquad (4).$$

The participation of EO groups in the surfactant molecule investigated, expressed as a percentage of EO groups in the particular surfactant (P / %), is given in Figure 3.

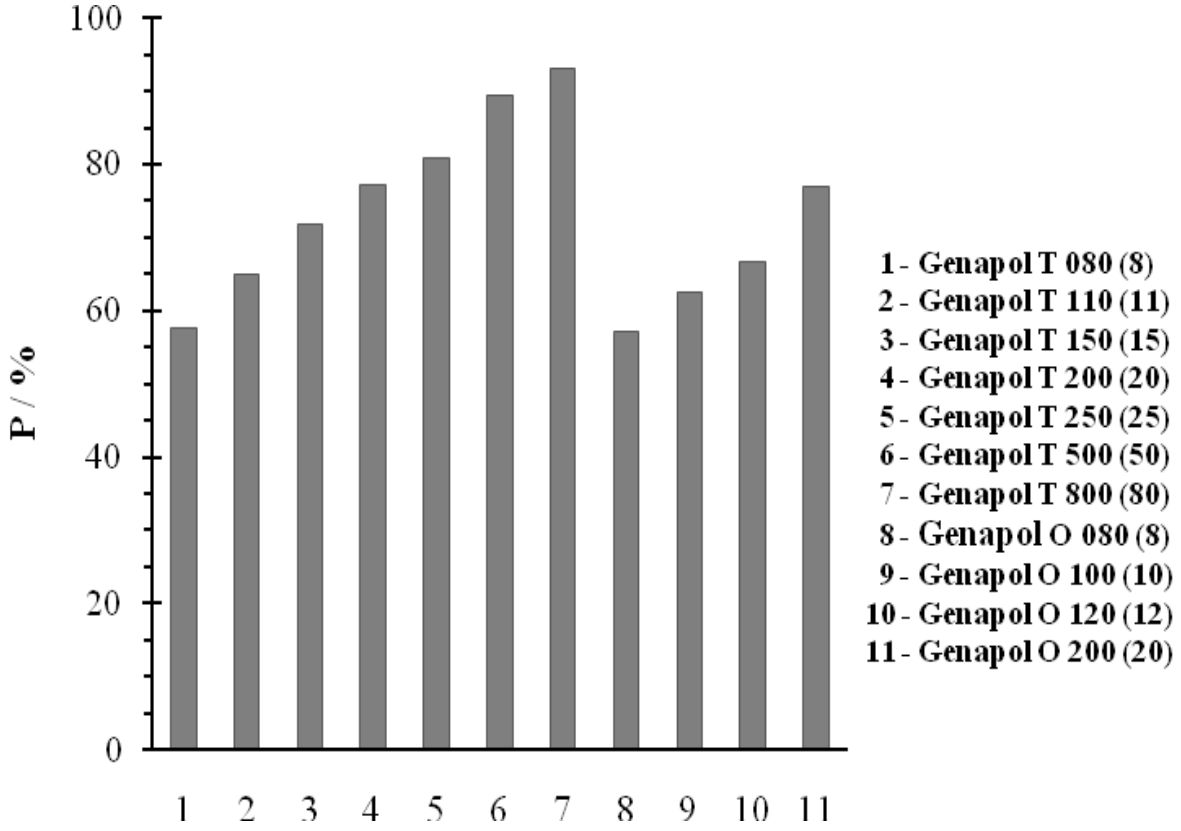


Figure 3. Participation of EO groups in surfactant molecules investigated (P / %). The values in parenthesis within the figure legend refer to EO group numbers of the particular surfactant.

3.4.1. Titration of homologous tallow fatty alcohol ethoxylates

A series of polyethoxylated tallow fatty alcohols containing 8 to 80 EO groups, most frequently used in liquid and powdered household and industrial detergent formulations, have been titrated potentiometrically using the DMI-TPB sensor described. The resulting potentiometric titration curves are shown in Fig. 4. The analyte concentrations for these investigations were on the order of 10^{-4} M.

The change in EMF value at the inflexion of the titration curves increased with increasing numbers of EO groups on the surfactant molecule. By titration of surfactants with a lower number of EO groups, symmetric titration curves were obtained, while those of surfactants with higher EO group numbers were more asymmetric.

The degree of asymmetry increased with increasing numbers of EO groups. The titration curves exhibited well defined and sharp inflexions, which facilitated a common end-point location using the first derivative method.

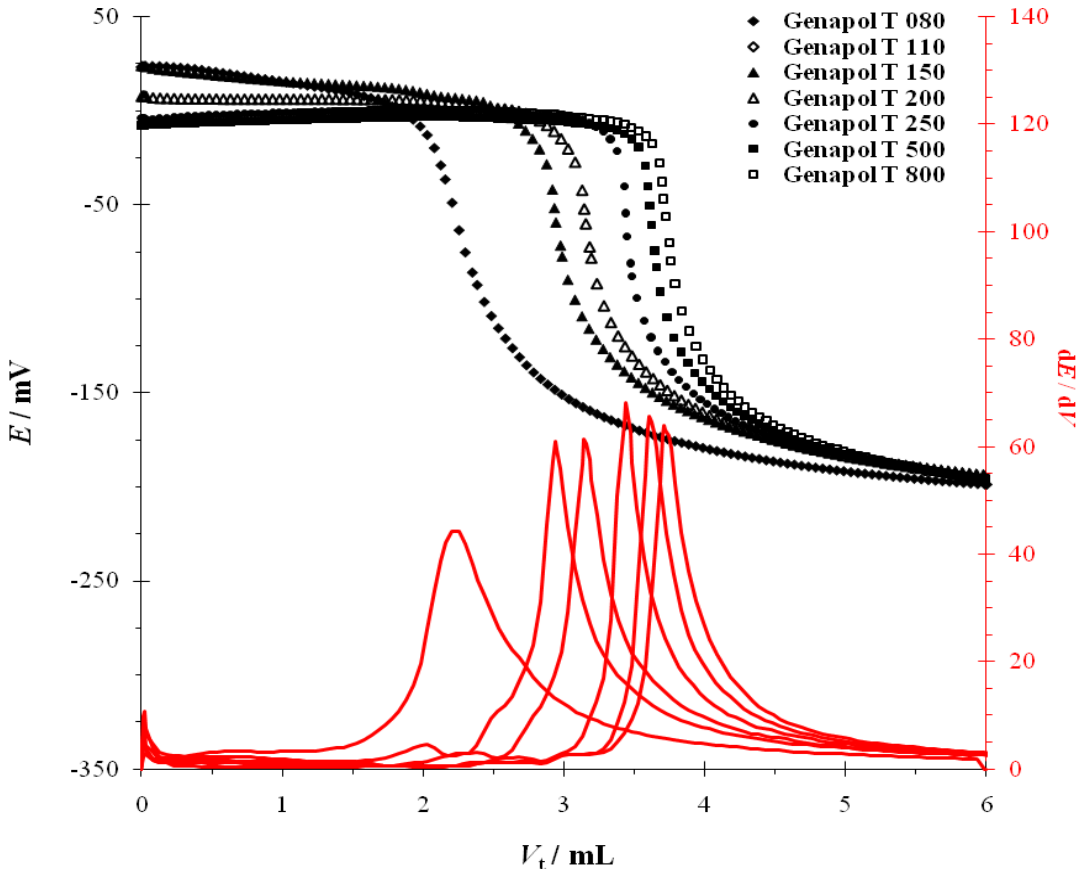


Figure 4. Titration curves and their first derivatives of the homologous series of ethoxylated tallow fatty alcohols using 5 mM sodium tetraphenylborate as the titrant. The mass concentration of EONS was the same in this titration and in the others.

3.4.2. Titration of homologous oleyl alcohol ethoxylates

A series of homologous oleyl alcohol ethoxylates containing 8 to 20 EO groups, which were primarily used as wetting and cleaning agents in different industrial detergent formulations, have been titrated potentiometrically using the same sensor. The resulting potentiometric titration curves are shown in Fig. 5.

The more pronounced inflexions were also obtained for surfactants containing higher number of EO groups on the surfactant molecule. The titration curves exhibited an almost symmetric shape compared to the formerly described polyethoxylated tallow fatty alcohols.

The results of the potentiometric titrations of some technical grade homologous oleyl alcohol ethoxylates and C_{16}/C_{18} - fatty alcohol ethoxylates are given in Table 1. The accuracy of determination (98.6 % - 100.8 %) can be considered satisfactory for the EONS determination.

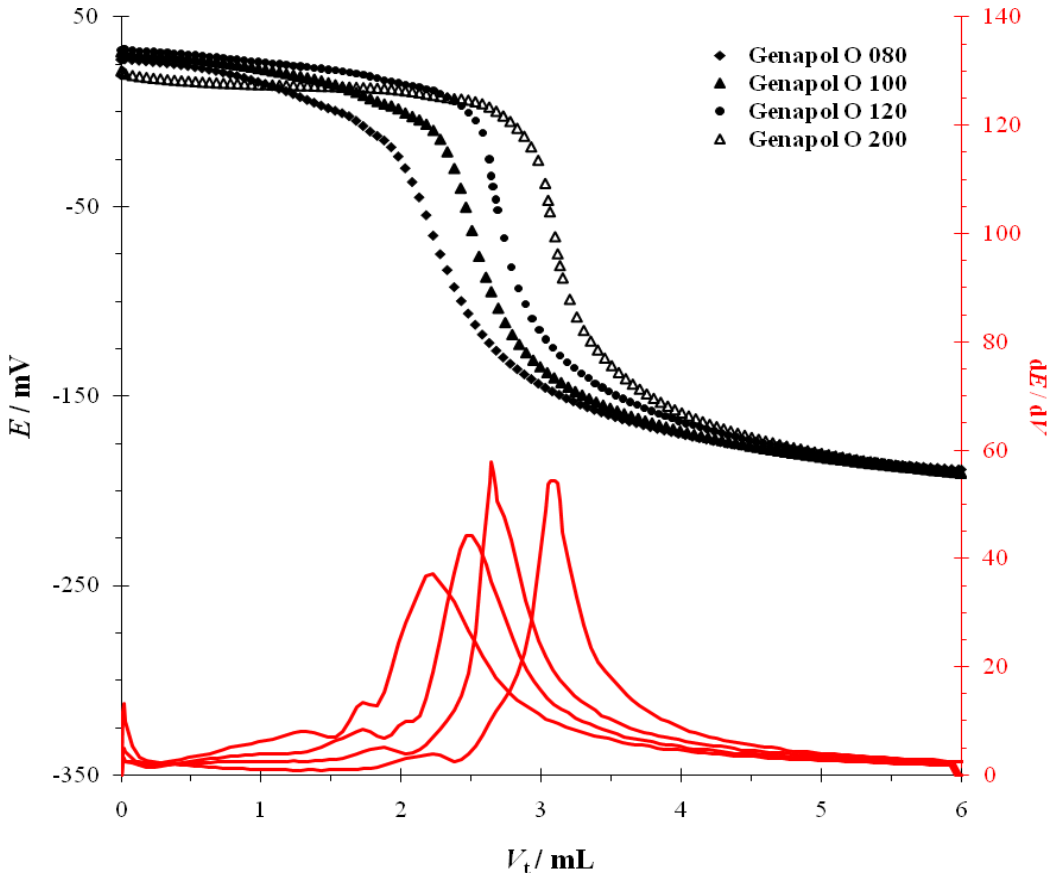


Figure 5. Titration curves and their first derivatives of the oleyl alcohol polyethoxylated nonionic surfactants using 5 mM sodium tetraphenylborate as titrant.

Table 1. Results of potentiometric titrations of some technical grade homologous of oleyl alcohol polyglycol ethers and C_{16}/C_{18} - fatty alcohol polyglycol ethers, using a DMI-TPB sensor as the indicator and NaTPB (c = 5 mmol/L) as the titrant.

SURFACTANT INVESTIGATED	EF*	EONS expected (mg)	EONS found**		
			(mg)	RSD (%)	Recovery (%)
Genapol O 080	2.268	5.00	5.04	1.100	100.8
Genapol O 100	2.016	5.00	4.97	0.572	99.4
Genapol O 120	1.866	5.00	4.96	0.558	99.2
Genapol O 200	1.579	5.00	4.95	0.482	99.0
Genapol T 080	2.262	5.00	5.02	0.956	100.4
Genapol T 110	1.901	5.00	4.97	0.422	99.4
Genapol T 150	1,681	5.00	4.93	0.505	98.6
Genapol T 200	1.468	5.00	4.95	0.504	99.0
Genapol T 250	1.453	5.00	4.96	0.668	99.2
Genapol T 500	1.355	5.00	4.97	0.530	99.4
Genapol T 800	1.333	5.00	4.95	0.794	99.0

*Experimental factor for EONS determination [mg EONS/mL NaTPB (c_{NaTPB} = 5 mmol/L)]
**Average of 5 determinations

3.4.3. Titration stoichiometry

Due to the complex reaction stoichiometry (Equation 2 and 3), the EONS content was usually calculated using the stoichiometric factor (F), which represented the number of EO groups reacting with one mole of TPB. One barium ion was determined to form a complex with 10-12 EO groups; thus, the stoichiometric factor should be between 5 and 6. The calculated values of the stoichiometric factors (Table 2) agreed with the data previously reported [18,23].

Table 2. Results of stoichiometric factors F (*n*EO/*n*TPB) calculated on the basis of the potentiometric titrations of selected analytical grade EONS and technical grade EONS homologues, using DMI-TPB sensor as the indicator and NaTPB (*c* = 5 mmol/L) as the titrant.

SURFACTANT INVESTIGATED		Mean number of EO groups	Mean M_r declared	F (*n*EO/*n*TPB)
CHEMICAL NAME	TRADE NAME			
Analytical grade EONS*:*				
Octylphenol decaethylene glycol ether	Triton X-100	10	647	5.70
Polyethylene glycol (23) lauryl ether	Brij 35	23	1200	6.64
Technical grade EONS *homologous:*				
Oleyl alcohol polyglycol ethers:	Genapol O 080	8	615	5.90
	Genapol O 100	10	703	5.74
	Genapol O 120	12	791	5.66
	Genapol O 200	20	1143	5.59
C_{16}/C_{18} - fatty alcohol polyglycol ethers:	Genapol T 080	8	610	5.93
	Genapol T 110	11	745	5.61
	Genapol T 150	15	920	5.48
	Genapol T 200	20	1140	5.40
	Genapol T 250	25	1360	5.34
	Genapol T 500	50	2460	5.51
	Genapol T 800	80	3780	5.64

4. CONCLUSIONS

A PVC liquid membrane surfactant sensor based on 1,3-didecyl-2-methylimidazolium-tetraphenylborate as an electroactive recognition element and bis(2-ethylhexyl) phthalate as a plasticizer was used for the potentiometric titration of the homologous tallow fatty alcohol and oleyl alcohol ethoxylates. The change in EMF value at the inflexion of the titration curves increased with increasing numbers of EO groups on the surfactant molecule for both, the tallow fatty alcohol and oleyl alcohol ethoxylates. The degree of asymmetry of the titration curves increased with increasing numbers of EO groups for tallow fatty alcohol ethoxylates, whereas the titration curves exhibited an almost symmetric shape for oleyl alcohol ethoxylates. The reaction stoichiometry of the EONS and barium ion complexes as well as the titration of the formed pseudocationic complex with tetraphenylborate was also studied.

ACKNOWLEDGEMENTS

This study was based on work financed by the Croatian Science Foundation and Saponia, Chemical, Pharmaceutical and Foodstuff Industry, Osijek.

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