Metrohm

Application Bulletin 305/2 e

Check of surfactant electrodes

Branch

General analytical chemistry, private laboratories; organic chemistry, chemistry; pharmaceutical industry; metals, electroplating; detergents, surfactants, cosmetics, fine chemical industry.

Keywords

Anionic surfactants; cationic surfactants; NIO electrode; Ionic Surfactant electrode; Cationic Surfactant electrode; Surfactrode Resistant; Surfactrode Refill; 6.0507.010; 6.0507.120; 6.0507.130; 6.0507.140; 6.0507.150; branch 1; branch 3; branch 4; branch 10; branch 12

Summary

This Application Bulletin describes some methods for testing the condition of electrodes for surfactant titrations. For testing Ionic Surfactant electrodes, sodium dodecyl sulfate (SDS) is titrated with TEGO®trant; for Cationic Surfactant electrodes TEGO®trant is titrated with SDS.

For NIO surfactant electrodes, PEG 1000 is titrated with sodium tetraphenylborate (STPB). For testing Surfactrode Resistant and Surfactrode Refill electrodes, titrations of SDS with TEGO®trant are performed. The criteria for the quality check are the height of the potential jump and the shape of the titration curve.

Instruments

- Titrator with DET mode
- 20 mL buret
- Rod stirrer
- Tiamo 2.4 or newer

Electrodes

NIO Surfactant electrode	6.0507.010
Ionic Surfactant electrode	6.0507.120
Cationic Surfactant electrode	6.0507.150
Surfactrode Resistant	6.0507.130
Surfactrode Refill	6.0507.140
Reference electrodes and electrolyte solutions	See in the corresponding chapters of the surfactants

Ionic /NIO surfactant electrodes

Table 1: Solutions for checking the ionic and NIO surfactant electrodes

Electrode	Ionic	Cationic	NIO
Sample	SDS	TEGO®trant	PEG1000
Titrant	TEGO®trant	SDS	STPB
Solvent	-	H_2O	H_2O
Auxiliary solution	-	-	$BaCl_2$

Ionic Surfactant and Cationic Surfactant electrodes

Reference electrode

LL ISE Reference Electrode filled with c(KCl) = 3 mol/L	6.0750.100

Reagents, buffers and solvents

- Buffer solution pH = 3.0 citrate/HCl
- TEGO®trant A 100: Metrohm No.: 6.2317.000 (6 g) or 6.2317.010 (60 g)
- Sodium dodecyl sulfate, SDS, CAS: 151-21-3
- Methanol, MeOH, puriss p.a.
- Formaldehyde solution, w(HCHO) = 35%

Titrants

c(TEGOtrant) = 0.005 mol/L	2.12 g TEGO®trant A100 is dissolved in a 1 L volumetric flask in approx. 800 mL water while stirring and filled up to the mark with deion. H_2O. The solution is carefully transferred to the buret. The solution must be allowed to stand in the filled buret and the tubing for at least one day before use. Prior to use, the whole buret volume is ejected and replaced with fresh solution.
c(SDS) = 0.005 mol/L	1.45 g SDS (>99 %) is weighed into a 1 L volumetric flask and dissolved in approx. 500 mL dist. water while stirring. After addition of 10 mL w(HCHO) = 35%, the flask is filled up to the mark with deion H_2O. The solution is carefully transferred to the buret. The solution must be allowed to stand in the buret and tubing for at least one day before use. Prior to use, the whole buret volume is ejected and replaced with fresh solution.

NIO Surfactant electrode

Reference electrode

Ag/AgCl Reference Electrode filled with c(NaCl) = 3 mol/L	6.0726.100

Reagents, buffers and solvents

- Boric acid, H_3BO_3, CAS: 10043-35-3
- Sodium tetraphenyl borate, STPB, CAS: 143-66-8
- Sodium hydroxide, c(NaOH) = 1 mol/L
- Polyethylene glycol, PEG 1000, CAS. 25322-68-3
- Barium chloride, $BaCl_2$, CAS: 10361-37-2 or 10326-27-9
- Polyvinyl alcohol, PVA, CAS: 9002-89-5
- Hydrochloric acid conc, HCl, CAS: 7647-01-0

Titrants

Titrant c(STPB) = 0.01 mol/L:	3.4223 g STPB is weighed into a beaker and dissolved in 300 mL deion. H_2O. In another beaker, 10 g polyvinyl alcohol is dissolved in 300 mL deion. H_2O while warming up. After cooling down, both solutions are rinsed into a 1 L volumetric flask, 10 mL buffer solution pH = 10.0 is added and the volumetric flask is filled up to the mark with deion. H_2O. The solution is carefully transferred to the buret. The solution must be allowed to stand in the filled buret and tubing for at least one day before use. Prior to use, the whole buret volume is ejected and replaced with fresh solution.
Buffer solution pH = 10.0	1.24 g H_3BO_3 is dissolved in deion. H_2O, 10 mL c(NaOH) = 1 mol/L is added to the solution and filled up to 100 mL with deion. H_2O.
c(PEG 1000) = 1 g/L:	1 g of PEG1000 is dissolved in a 1 L volumetric flask by stirring (not shaking!) and filled up to the mark with deion. H_2O. The solution is carefully transferred to the buret. The solution must be allowed to stand in the filled buret and tubing

	for at least one day before use. Prior to use, the whole buret volume is ejected and replaced with fresh solution.
c($BaCl_2$) = approx. 0.1 mol/L (Auxiliary solution)	21 g $BaCl_2$ or 25 g $BaCl_2 \cdot 2\ H_2O$ is dissolved in dist. water, 1 mL conc. HCl is added and the solution filled up to 1 L with deion. H_2O.

Analysis

The analysis is performed in two triplicates respectively. The first triplicate serves for the conditioning of the electrode and the obtained results are not taken into account. The next triplicate is evaluated.

Parameters for the appropriate DET titrations are listed in table 2.

Ionic Surfactant electrodes

A 150 mL beaker is filled with 10.00 mL c(SDS) = 0.005 mol/L, 5 mL methanol, 10 mL buffer solution pH = 3.0 and approx. 50 mL dist. H_2O. The titration is carried out under vigorous stirring with c(TEGOtrant) = 0.05 mol/L until after the equivalence point.

Cationic Surfactant electrodes

A 150 mL beaker is filled with 10.00 mL c(TEGOtrant) = 0.005 mol/L, 10 mL methanol, 10 mL buffer solution pH = 3.0 and approx. 50 mL dist. H_2O. The titration is carried out under vigorous stirring with c(SDS) = 0.005 mol/L until after the equivalence point.

NIO Surfactant electrodes

A 150 mL beaker is filled with 20 mL c(PEG 1000) = 1.0 g/L, 10 mL c($BaCl_2$) = 0.1 mol/L and 50 mL dist. water. The solution is then titrated under vigorous stirring with c(STPB) = 0.01 mol/L until after the equivalence point.

Table 2: Titration parameters for ionic / cationic and NIO Surfactant electrode testing

Electrode	"Ionic / Cationic" Surfactant	NIO
Mode	DET U	DET U
Pause	30 s	30 s
Signal drift	50 mV/min	50 mV/min
Max. waiting time	60 s	60 s
Measuring point density	0	2
Min. increment	50 µL	50 µL
Stop volume	12 mL	12 mL
EP criterion	20	20
EP recognition	all	all
Fixed endpoint evaluation	Yes	Yes
Fixed endpoint quantity	Volume	Volume
Fixed value 1	$V_{EP1} \times 0.9$	$V_{EP1} \times 0.9$
Fixed value 2	$V_{EP1} \times 1.1$	$V_{EP1} \times 1.1$

Surfactrode Resistant and Surfactrode Refill electrode

Table 3: Solutions for testing the Surfactrodes

Electrode	Surfactrode Resistant	Surfactrode Refill
Sample	SDS	SDS
Titrant	TEGO®trant	TEGO®trant
Solvent	MIBK/EtOH/H_2O	MIBK/EtOH/H_2O
Auxiliary solution	TEGO add	TEGO add

Reference electrode

Ag/AgCl Reference Electrode filled with c(KCl) = 3 mol/L	6.0726.107

Reagents, buffers and solvents

- TEGO®trant A 100: Metrohm Nr.: 6.2317.000 (6 g) or 6.2317.010 (60 g)
- Sodium dodecyl sulfate, SDS, CAS: 151-21-3
- Methyl isobutyl ketone, MIBK, puriss. p.a, CAS: 108-10-1
- Ethanol, EtOH, puriss. p.a
- Hydrochloric acid, c(HCl) = 0.5 mol/L
- Formaldehyde solution, w(HCHO) = 35%

Titrants

c(TEGOtrant) = 0.005 mol/L	2.12 g TEGO®trant A100 is dissolved in a 1 L volumetric flask in approx. 800 mL deion. H_2O while stirring (not shanking!) and filled up to the mark with deion. H_2O. The solution is carefully transferred to the buret. The solution must be allowed to stand in the buret for at least one day before use. Prior to use, the whole buret volume is ejected and replaced with fresh solution.
c(SDS) = 0.005 mol/L	1.45 g SDS (>99 %) is weighed into a 1 L volumetric flask and dissolved in approx. 500 mL deion. H_2Owhile stirring (not shaking!). After addition of 10 mL w(HCHO) = 35%, the flask is filled up to the mark with deion. H_2O. The solution is carefully transferred to the buret. The solution must be allowed to stand in the filled buret for at least one day before use. Prior to use, the whole buret volume is ejected and replaced with fresh solution.
Solvent mixture	MIBK/Ethanol 1:1 (vol/vol)

Analysis

The analysis is performed in two triplicates respectively. The first triplicate serves for the conditioning of the electrode and the results are not taken into account. The next triplicate results are evaluated.

Parameters for the DET U titrations are listed in table 4.

A 150 mL beaker is filled with 10 mL c(SDS) = 0.005 mol/L and 50 mL deion. H_2O. The pH value of the solution is adjusted to pH 2 (Surfactrode Refill) or pH 3 (Surfactrode Resistant) with c(HCl) = 0.5 mol/L. Then 20 mL solvent mixture and 0.2 mL TEGO add are added and titrated under vigorous stirring with c(TEGOtrant) = 0.005 mol/L until after the equivalence point.

Table 4: Titration parameters for Surfactrode Resistant and Surfactrode Refill

Electrode	Surfactrode Resistant	Surfactrode Refill
Mode	DET U	DET U
Pause	60 s	30 s
Signal drift	10 mV/min	10 mV/min
Max. waiting time	120 s	120 s
Measuring point density	0	2
Min. increment	150 µL	50 µL
Stop volume	16 mL	16 mL
Fixed endpoint evaluation	Yes	Yes
Fixed endpoint quantity	Volume	Volume
Fixed value 1	V_{EP1} × 0.9	V_{EP1} × 0.9
Fixed value 2	V_{EP1} × 1.1	V_{EP1} × 1.1

Evaluation for all surfactant electrodes

Evaluation criteria

- The relative standard deviation of the threefold determined values (n = 3) should be less than 1.0%.
- Only one EP should be found.
- The titration curve should have a good symmetrical S-shape (see examples attached).
- The potential jump difference $\Delta U_{90\text{-}110\%}$ must exceed 70 mV.

Calculation for potential jump

The potential jump is calculated as following: In the DET U command under “Additional evaluations” the checkbox “Fixed endpoint evaluation” must be activated and the endpoints can be calculated according to the formulas (1, 2) below (***tiamo***™ is necessary).

$FP_1 = V_{EP1} \times 0.9$ (1)

$FP_2 = V_{EP1} \times 1.1$ (2)

V_{EP1}: Titrant volume used until first equivalence point in mL
FP_1: Fixed endpoint 1 in mL
FP_2: Fixed endpoint 2 in mL

In the calculation command the following formula has to be entered.

$\Delta U_{90\text{-}100} = |U_{FP2} - U_{FP1}|$

$\Delta U_{90\text{-}110\%}$: Potential jump difference
Absolute value of $FP_2 – FP_1$ in mV
U_{FP1}: Measured value at fixed endpoint 1 in mV
U_{FP2}: Measured value at fixed endpoint 2 in mV

Comments

- An electrode that measures an incorrect value is defective or contaminated in some way. Directions for cleaning of such electrodes are given in the corresponding instructions for use and monographs.
- Surfactants are strongly substantive, i.e. they absorb onto surfaces. For this reason the buret and the tubing should be filled with the titrant one day before the determination. This ensures that all surfaces are saturated. For the same reason, the same bottles and beakers should be used for the solutions and titration.
- For two-phase titrations a very good mixing of the sample during titration is essential. It is really important that both phases are very well mixed and an emulsion is formed without getting air bubbles in the solution or forming a vortex. A magnetic stirrer is not sufficient for mixing, a rod stirrer has to be used.

List of abbreviations

SDS	Sodium dodecyl sulfate / Sodium lauryl sulfate
PEG	Polyethylene glycol
MIBK	Methyl isobutyl ketone / Isobutyl methyl keton
STPB	Sodium tetraphenyl borate

Example determinations

Ionic Surfactant electrode

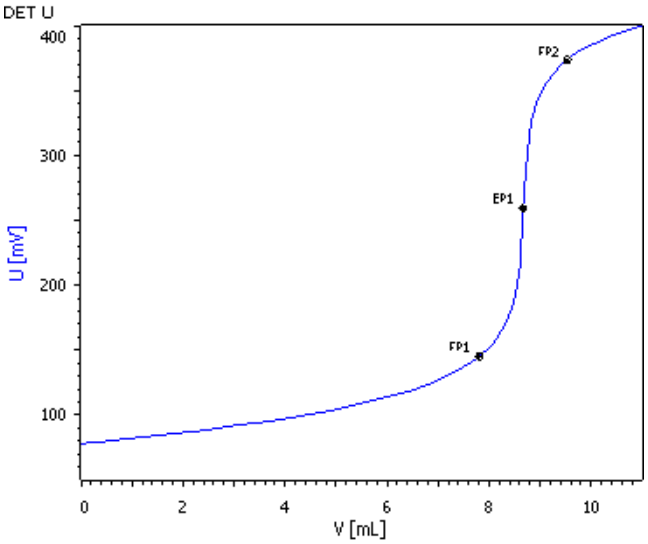

Fig. 1: Titration of SDS with TEGO®trant using the Ionic Surfactant electrode

Cationic Surfactant electrode

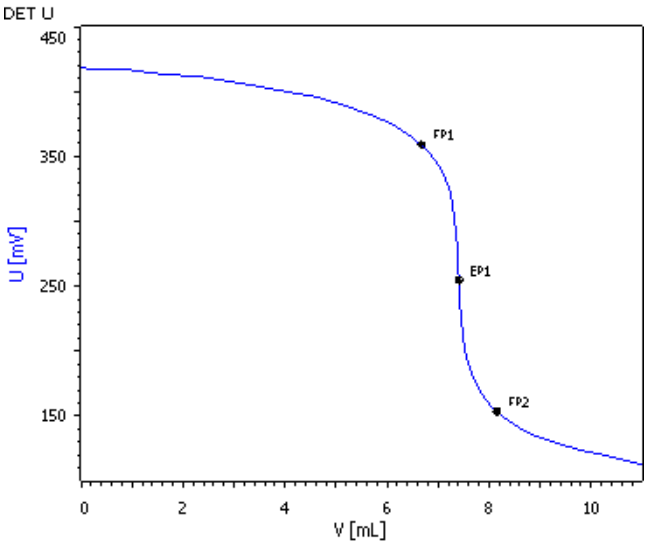

Fig. 2: Titration of TEGO®trant with SDS using the Cationic Surfactant electrode

NIO Surfactant electrode

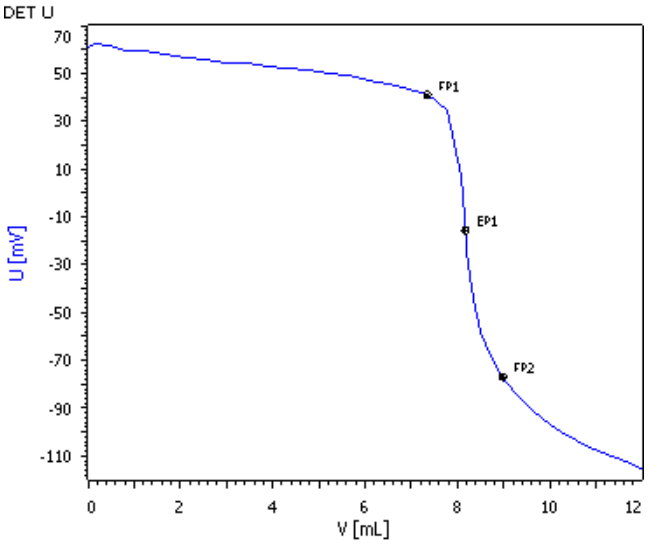

Fig. 3: Titration of PEG1000 with STPB using the NIO Surfactant electrode

Surfactrode Resistant

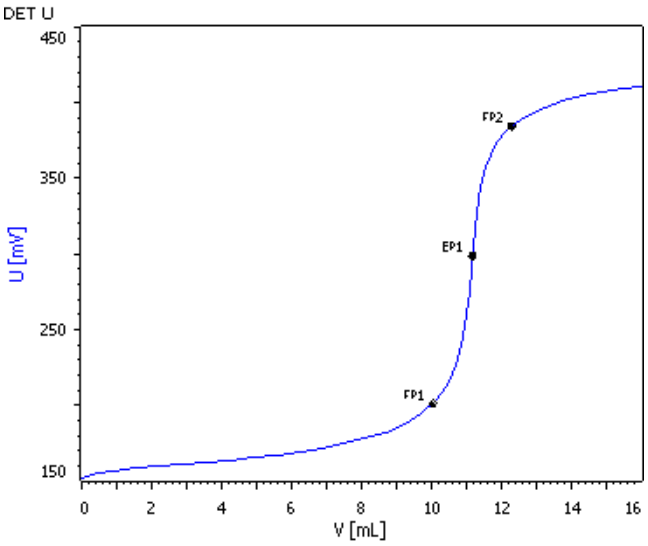

Fig. 4: Titration of SDS with TEGO®trant using the Surfactrode Resistant

Surfactrode Refill

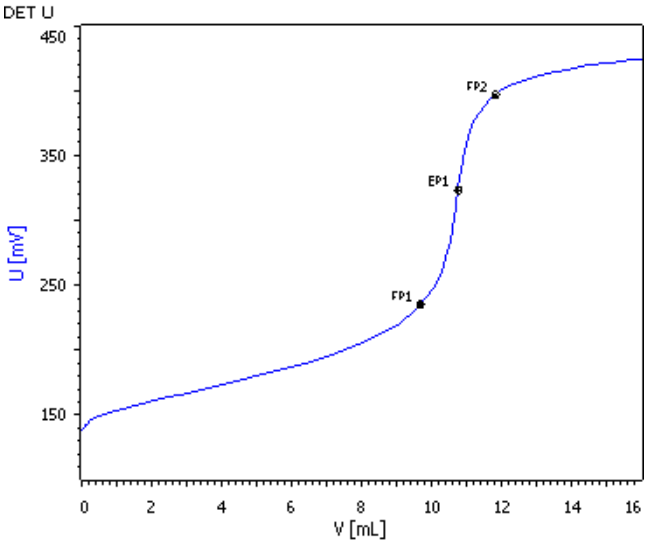

Fig. 5: Titration of SDS with TEGO®trant using the Surfactrode Refill

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Competence Center Titration

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