Titration of nonionic surfactants

Description

Non-ionic surfactants are widely used in detergents and cleaning agents as well as process aids as wetting agents and emulsifiers. Nonionic surfactants consist of one or more non-polar parts (mostly hydrocarbon chains) and a polar part. The polar part usually consists of polyethylene (EO) - or polypropylene glycols (PO) or combinations of EO and PO. Surfactants with polyglucoside chains or alkynediol groups are also available. The method described here is only suitable for surfactants with ethylene oxide chains or EO / PO combinations with a sufficiently high EO content.
The content can be determined by titration with an anionic precipitant (sodium tetraphenylborate, STPB). For this, a barium chloride solution is added to the sample. The Ba^{2+} ions form cationic complexes with the EO chains of the surfactants, which form poorly soluble, hydrophobic adducts with the anionic STPB. Non-ionic surfactants with a carbon chain <C10 or less than 5 EO units are usually not fully detected.
The composition of the Ba^{2+} / surfactant complexes is not uniform and depends on the surfactant, so the precipitation reaction is not stoichiometric. Therefore, for each surfactant a factor should be determined with a solution of known content.
Since the hydrophobic adducts are often quite sticky and can settle on the electrodes, solutions should be diluted as possible (0.004 mol/L – 0.01 mol/L). Polyvinyl alcohol or gum arabic can help to keep the electrodes clean.
STPB also forms poorly soluble precipitates with K^+, because of that the electrolyte of the reference electrode must be potassium-free - a NaCl solution is usually used.
The pH is not critical, but should be in the slightly acidic state to avoid the precipitation of $Ba(OH)_2$.
Polyethylene glycols, potassium salts and various anionic and cationic surfactants can interfere with the titration. A high content of sulfate ions can also disturb because the precipitation of $BaSO_4$.

Devices

Titrator	TL 7000 or higher
Exchange unit	WA 10
Electrode	TEN 1100 PLH
Reference Electrode	B 2420+ (NaCl – electrolyte)
Cable	L 1 A + L 1 N
Lab accessoires	Magnetic stirrer TM 235
	Glass beakers 150 oder 250 ml

Reagents

1	Sodium tetraphenylborate (STPB) 0.004 – 0.01 mol/L
2	Barium chloride – solution 0.1 mol/L
3	Sodium chloride - solution 3 mol/L
4	Gum Arabic
5	Polyvinylalkohol
6	Distilled water
7	Hyamin 1622 solution 0.004 mol/L
All reagents should be in analytical grade or better.	

Titration procedure

Reagents

Sodium tetraphenylborate (STPB) 0.01 mol/L
3.42 g Sodium tetraphenylborate (STPB) are dissolved in 0.9 L dist. Water and made up to 1.0 L.
The titer determination can be done with Hyamin 1622. Mostly a factor determination with the surfactant to be titrated is more suitable. See application note „Titer STPB_Sodiumtetraphenylborat“.

Barium chloride solution 0.1 mol/L
24.43 g of barium chloride dihydrate are dissolved in dist. Water and made up to 1 liter.

NaCl 3 mol / L
17.53 g of sodium chloride are dissolved in dist. Water and made up to 100 mL.

Polyvinyl alcohol 0.5%
0.5 g polyvinyl alcohol is placed into approx. 80 mL hot dist. water at 80-90° C and dissolved with stirring. After the solution has cooled down it is made up to 100 mL.

Gum arabic solution 5%
5 g gum arabic is placed into approx. 80 mL hot water at 80-90° C and dissolved with stirring. After the solution has cooled down, 1 ml of 30% formaldehyde is added and made up to 100 ml.

Cleaning and handling the electrodes

TEN 1100
The TEN 1100 electrode is rinsed with dist. water or a solution of Triton X in dist. Water. The membrane of the electrode must not be cleaned mechanically. Do not use solvents for cleaning, the membrane can be destroyed. Store the electrode clean and dry.
With a new electrode or one that has not been used for a long time, the potential jumps in the first titrations are usually quite flat. Therefore, the electrode should be conditioned before use. For this, the electrode is placed in a solution of 0.5 ml Hyamin 1622 (0.004 mol/L) and 0.2 mL Sodium tetraphenylborate (STPB) (0.01 mol/L) in 80mL Water.

B 2420+

The transport lock (the transparent silicone ring above the ground joint diaphragm) must be removed before use. The electrolyte in the electrode must be replaced with NaCl 3 mol/L. For this purpose, the refill opening is opened and the ground joint diaphragm is pushed upwards so that the electrolyte can flow out. The electrode is rinsed several times with NaCl 3 mol / L and then filled with the NaCl solution. The electrode is stored in NaCl 3 mol/L.

Sample preparation

The sample is weighed in, 10 ml barium chloride 0.1 mol/L and 1 ml polyvinyl alcohol 0.5% or gum arabic 5% are added. The mixture is made up to 150 ml with dist. water. In the case of alkaline samples, the pH must be adjusted to pH <7 with diluted HCl. The sample should contain approx. 5 - 50 mg (0.02 - 0.06 mmol) of non-ionic surfactant.

In the case of poorly soluble samples, the solubility of the sample can be improved by adding a little amount Methanol or Ethanol. Attention: Methanol and Ethanol reduce the life time of the electrode, the addition should not exceed 5%.

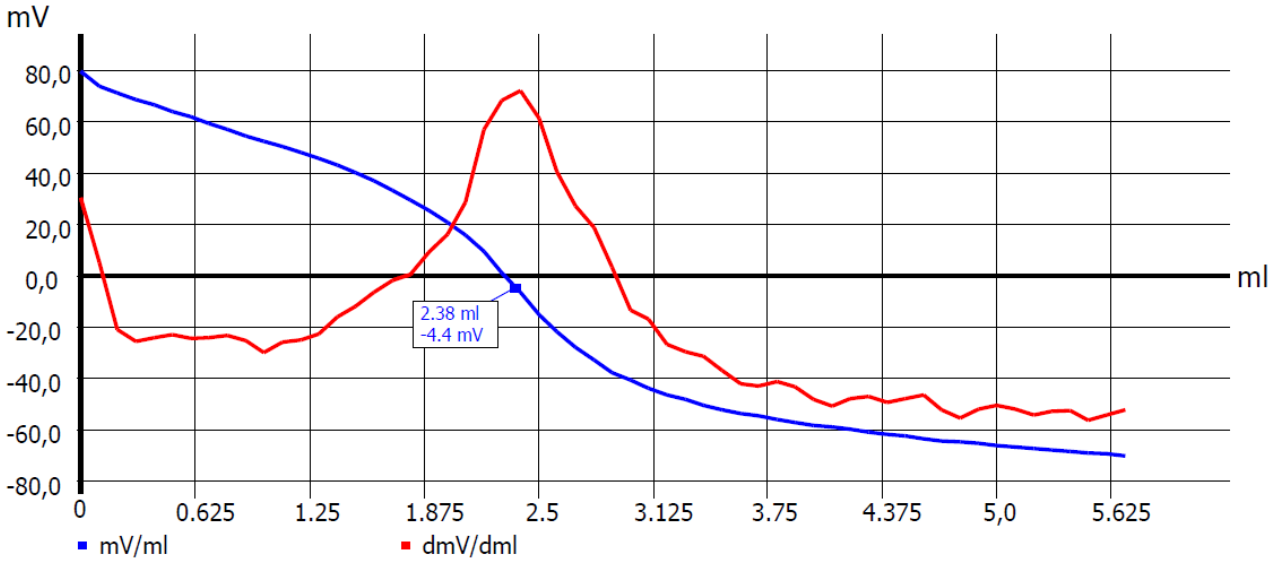
Then it is titrated to an equivalence point with Sodium tetraphenylborate (STPB). For some samples, the potential jump on the EQ is only weak. Here it is often better to use an end volume or the potential of a titrated sample as stop criteria.

If the content of surfactants or surfactant concentrates that contain large amounts of nonionic components should be determined, the required amount of sample is very small and difficult to weigh. Then the following method can be used: a larger amount of sample (W_{Sample}) is weighed into a flask. For this, 50 - 200 times the amount of distilled water (W_{H2O}) is weighed and the sample is dissolved in it. From this solution an aliquot A is taken for the titration. The amount of sample contained in the aliquot A is calculated using the following formula:

$$W\ [g] = \frac{W_{Sample}\ [g]}{(W_{Sample}\ [g] + W_{H2O}[g])} * A\ [g]$$

Titration parameter

For surfactant titration a slow, linear titration with relatively large steps is well suited.
Since it is a slow precipitation titration, slow measuring speeds are necessary.
Such a titration can last 10 to 20 minutes.



Default method	-		
Method type	Automatic titration		
Modus	Linear		
Measured value	mV		
Measuring speed / drift	User defined	Minimum holding time	8 s
		Maximum holding time	25 s
		Measuring time	4 s
		drift	3 mV/min
Initial waiting time	5 s		
Linear steps	0.1 mL		
Damping	average	Titration direction	decrease
Pretitration	off	Delay time	0 s
End value	off		
EQ	on	Slope value	80
Max. titration volume	10 mL		
Dosing speed	100%	Filling speed	30 s

For difficult samples with weak potential jumps, it can be advantageous to use a fixed waiting time of 20s or more instead of the measurement speed / drift.

Calculation:

For the calculation, either the concentration of the STPB solution in mol/L or a previously determined factor in mg/ml is used.

$$NIO\ [\%] = \frac{(EQ1 - B) * T * M * F1}{W * F2}$$

B	0	Blank value
EQ1		Consumption at first EQ
T	WA	Exact concentration of the titrant in mol/L
M	625	Molar mass of a nonionic surfactant
W	man	Sample weight [g]
F1	0.1	Conversion factor
F2	1	Conversion factor

In this example the result is calculated with a molar mass of 625 g/mol (~Triton X). For other surfactants, the corresponding molar mass must be used for the calculation.

Calculation with factor mg/ml:

$$NIO\ [\%] = \frac{(EQ1 - B) * T * M * F1}{W * F2}$$

B	0	Blank value
EQ1		Consumption at first EQ
T	WA	Factor of the titrant in mg/mL
M	1	Molar mass of a nonionic surfactant
W	man	Sample weight [g]
F1	0.1	Conversion factor
F2	1	Conversion factor

This calculation is done with a specific factor determined for the surfactant.

Any questions? Please contact the application team:

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