

RICE UNIVERSITY

Manual 2

Manual for Surfactant Titration

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2. Surfactant Titration

Titration is an efficient and economic method to measure the surfactant concentration. Two phase titration and potentiometric titration are the two main methods used widely. Two phase titration has a relatively simple process requiring only a modest assembly of apparatus, however, it has a number of inherent problems, such as difficult to judge of the end point location, time consuming, hazard to health by using organic solvents, ect. Potentiometric titration has been shown to overcome most of these problems, so this manual will focus on develop suitable procedure for measuring the surfactant concentration by potentiometric titration.

2.1 Equipment

Titration: 716 DMS Titration connected to a computer is used for automatic titration and data collection.

Surfactant Electrode: an ion selective electrode (ISE, pHoenix, Cat. No. SUR1502) is used for aqueous surfactant titration and its electrolyte solution is 4M KCl (Cat. No. R0010011).

2.2 Materials

2.2.1 Titrant (1000ml)

The concentration of titrant needed for analysis can be determined from the table below.

Table 2-1 Recommended Titrant Concentrations

Recommended Titrant Concentration (M)	Expected Sample Concentration (M)
0.05	0.05 to 0.001
0.005	0.001 to 0.0001
0.001	0.0001 to 0.00001

Titrant for anionic surfactants was Hyamine 1622 (from Fisher Scientific), suggested by electrode manual¹. Here another titrant, 1,3-didecyl-2-methylimidazolium chloride (TEGO ® trant A100 from Fisher Scientific) is used and its advantage will be introduced in 2.4.3.

Titrant for cationic surfactants is anionic surfactant, such as sodium dodecyl sulfate (SDS), which will be shown at the end of this manual. However, this manual will more focuses on studying the titration of anionic surfactants.

2.2.2 Calibration Solution

SDS and hyamine aqueous solutions are the calibration solution for the anionic and cationic surfactant titrations, respectively (from Fisher Scientific). The concentration of the calibration solution is two times of the concentration of titrant. For example, if $C_{\text{titrant}} = 0.001 \text{ M}$, then $C_{\text{SDS}} = 0.002 \text{ M}$.

2.2.3 Solutions for electrode maintenance

Sample Additive, diluted Triton X-100 keeps electrodes clean when added to samples. 1ml Triton X-100 is diluted to 1 Liter by DI (0.1 wt% Triton X-100)

Reconditioning Solution, 0.0001M SDS aqueous solution was suggested by the electrode manual¹. Another more efficient ionic surfactant will be introduced and compared with SDS in 2.4.1.

pH Adjuster Solutions, 0.01 M HCl for adjusting the pH of both anionic and cationic surfactant, suggested by the electrode manual¹.

Electrode Rinse Solution, 0.005M HCl for acidic rinse for anionic or cationic surfactant analysis suggested by the electrode manual¹.

2.2.4 Surfactant Sample

Surfactant sample should be diluted within the range of 10^{-2} - 10^{-5} M to get accurate result. Concentrations between 10^{-4} - 10^{-5} M help preserve electrode life. Corresponding titration concentration is selected according to Table 2-1.

For every 50 ml of sample, use 1ml of Triton X-100 described in 2.2.3.

Adjust pH to 2.5 to 4.5 for anionic surfactants, to 3.0 for cationic surfactants by addition of pH Adjuster Solutions described in 2.2.3.

2.3 Procedure

2.3.1 Conditions for the Electrode¹

Preparing the electrode for a titration

- Open the filling hole.
- Fill the electrolyte solution.
- Soak the tip of the electrode in reconditioning solution for 10 minutes before first time using. Use fresh solution daily.
- Clean the electrode with DI water.
- Precondition electrode in DI water for 10 min.
- The surfactant electrode has an operating pH range of 2-12. Use at other pH values can adversely affect the membrane.

Between titrations

- Keep the filling hole open during the titration.
- Use Acid Rinse Solution described in 2.2.3 to rinse the electrode and blot dry with a soft, lint-free tissue before the titration.
- Clean the electrode with DI water.
- To prevent air entrapment, mount the electrode at a 20° angle from the vertical.
- Precondition electrode in DI water for 10 min between two titrations
- If the response becomes noisy, sluggish or irreproducible, soak in Reconditioning Solution for 30 minutes to recondition the electrode.

Storing the electrode

- Shorter storage periods: rinse the membrane element and cover the filling hole with the rubber sleeve; soak electrode in reconditioning solution.
- Storage periods longer than one month: rinse and dry the membrane element; drain the filling solution in the reference chamber; cover the filling hole with the rubber sleeve; cover the tip with protective cap.

2.3.2 Titration Parameters

Titrant is delivered by Dynamic Equivalence point Titration method² (Normal method in the computer). In this titration, the size of the volume increments varies as a function of the slope of the titration curve. The minimum increment is 20 μL ; Dosage rate is set as Maximum (ml/min), which is 3 times of the burette size; Signal drift is 2 mV/min and equivalent time is 20 s.

2.3.3 Titrant Calibration

Dilute 2 ml calibration solution (0.002 mol/L) into 50 ml by DI water. Adjust pH by 3ml **pH Adjuster Solutions** and add 1ml sample additive. The concentration of the titrant is measured by this calibration solution. Usually, the average value from three titration results is used as the titrant concentration.

2.3.4 Titration of Surfactant Sample

For optimizing the Ion Selective Electrode (ISE) performance:

1. Avoid the presence of organic solvents in the aqueous phase, please see details in 2.4.4
2. Reduce interfacial tension between the membrane and the solution by adding 1ml Triton X-100 solution to every 50 ml surfactant solutions
3. Keep the electrodes clean of reaction product
4. Reduce the amount of air bubbles in the system in general and adhering to the electrode by stirring samples at a constant speed, but slowly, to avoid foaming.
5. Suppress the formation of micelles by limiting surfactant concentration below CMC.

6. Lower the electrodes into the solution so that the tip is completely covered and wait until the mV reading is stable, that is, drift is +/- 1 to 2 mV/minute.
7. Adjust pH of the surfactant solution according to 2.2.4

Then start titration.

2.4 Discussion

2.4.1 Recondition

The electrode manual¹ suggests to reconditioning the electrode by the SDS solution (10^{-4} M) when the response becomes noisy, sluggish or irreproducible. It is found that titration result gets much better after the electrode is soaked in SDS solution for long time, such as overnight. For getting a more efficient way to reconditioning the electrode, another surfactant, C₁₂-o-xylene sulfonate sodium was tested. This surfactant will be called as C₁₂OXS in this manual. The C₁₂OXS gives larger potential jump around inflection point compared with SDS as shown in Figure 2-1.

For comparing the efficiency of these two reconditioning solutions, the electrode was tested by the following procedure: a) the electrode with bad performance was reconditioned by SDS for 30 minutes and then SDS was titrated; b) when the electrode got worse again after some tests, it was reconditioned by C₁₂OXS for 30 minutes and then SDS was titrated. The titration results from a) and b) are compared in Figure 2-2 and it is clear that the electrode reconditioned by C₁₂OXS gives better response. Same procedure was used to test C₁₂OXS and the results are shown in Figure 2-3. The results also show C₁₂OXS is a better reconditioning solution.

Therefore, C₁₂-o-xylene sulfonate sodium will be used as the reconditioning solution instead of SDS.

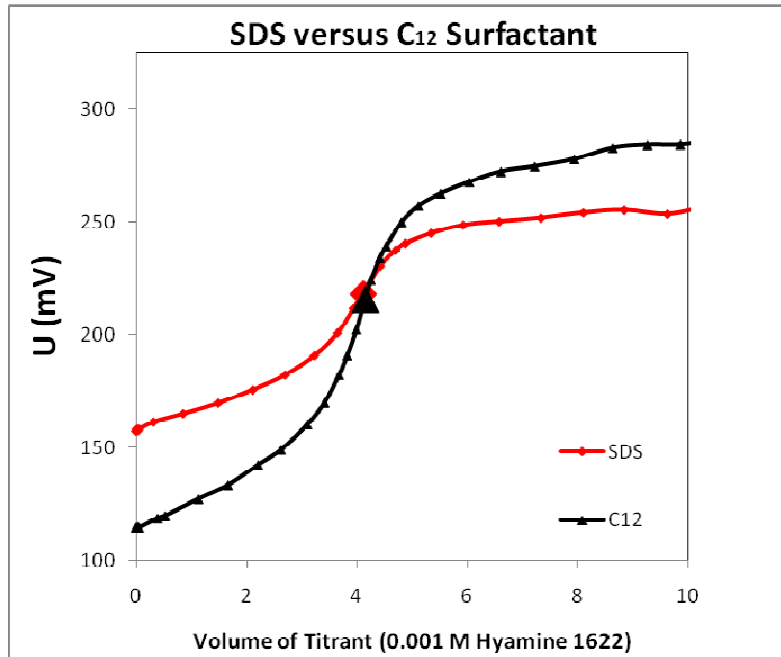


Figure. 2-1. Titration curves of SDS and C₁₂OXS

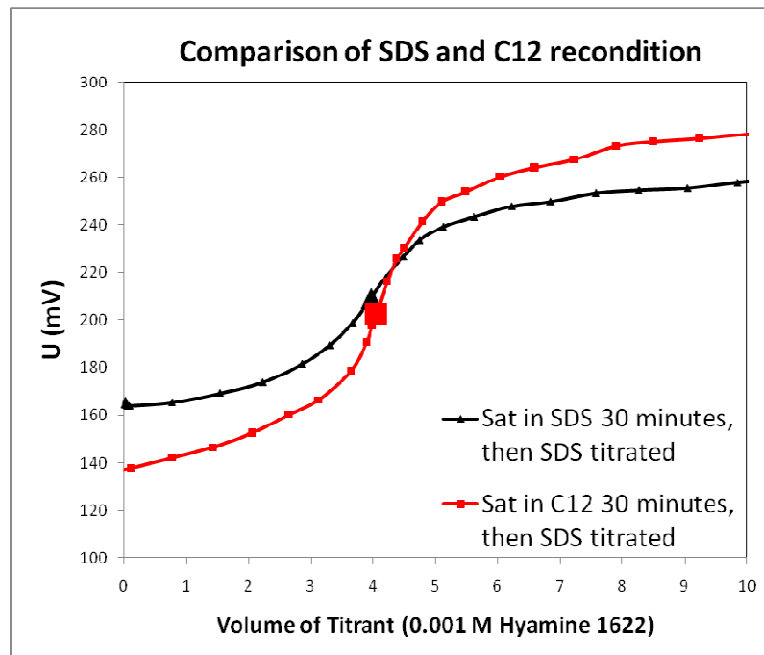


Figure 2-2. Titration curves of SDS after electrode reconditioned in different reconditioning solutions

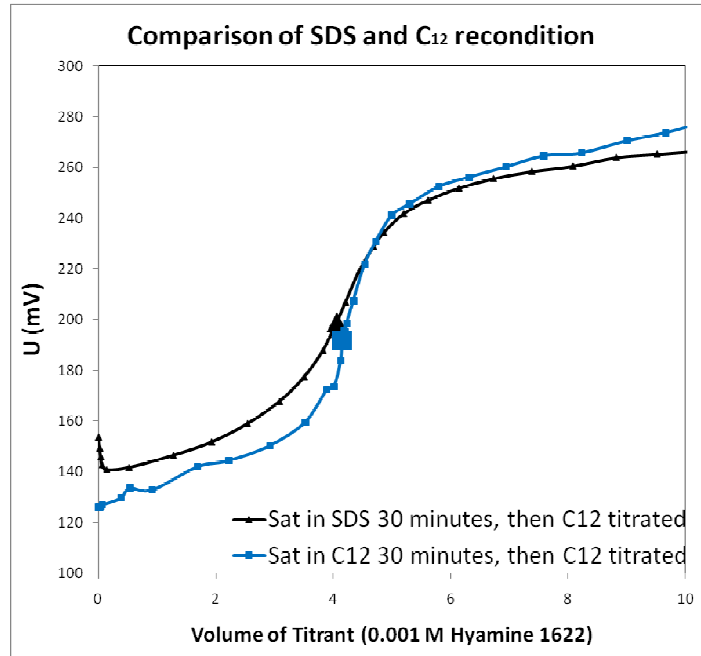


Figure. 2-3. Titration curves of C₁₂OXS after electrode reconditioned in different reconditioning solutions

2.4.2 Effect of Surfactant Carbon Chain Length

The surfactant carbon chain length affects the titration results, because the solubility of the surfactant cation-anion salt changes with its molecular weight. Here, four surfactants, C_n-Oxylene sulfonate sodium, were titrated by hyamine as shown in Figure 2-4. This series of surfactant will be called as C_nOXS in this manual. C₁₂OXS and C₂₄OXS give clear end points, however when the carbon chain becomes shorter, such as n= 8 and 9, no clear end point is present.

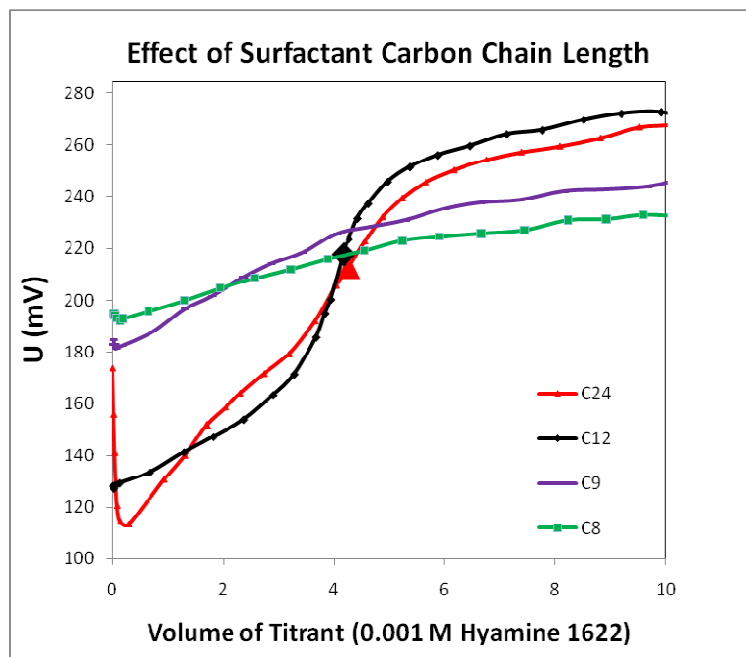


Figure 2-4. Titration curves for the surfactants with different chain length

2.4.3 Effect of Titrant Type

Although any cationic surfactant can be used as a titrant, however, the existence of some qualitative differences due to the titrant has been pointed out.³⁻⁶ For a given anionic surfactant, the potential jumps to equivalence increase as the solubility product of the anionic-cationic surfactant ion-pair lowers. Here, TEGO ® trant A100 is compared with Hyamine 1622 and it is clear that TEGO is a better titrant. However, TEGO is much more expensive than Hyamine and the price and source of these two titrants are shown below:

TEGO ® trant A100 **60g** ~ **\$831.04** from Fisher Scientific

Hyamine 1622 **50g** ~ **\$80.70** from Sigma-Aldrich

The molecular structures of TEGO and Hyamine are shown in Figure 2-5 and Figure 2-6, respectively. Both titrants were calibrated before using. Their performances were compared and the details are shown below.

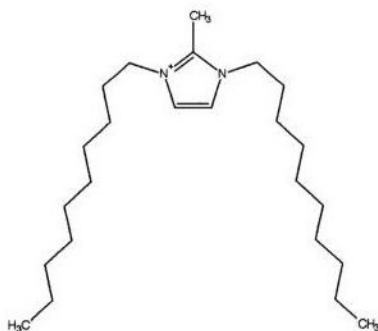


Figure 2-5. 1,3-didecyl-2-methyl imidazolium chloride (TEGO ® trant A100)

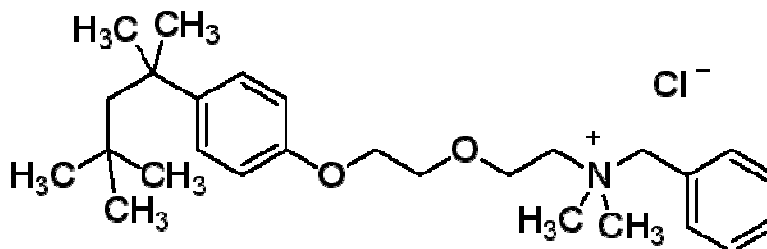


Figure 2-6. Octylphenoxyethoxyethyltrimethylbenzylammonium chloride (Hyamine 1622)

SDS calibrations

TEGO and hyamine were calibrated by SDS aqueous solution (0.00206 M). TEGO gives larger voltage change around the end point than hyamine as shown in Figure 2-7. Also, it was found that the activity of TEGO sample we have is around 90%.

Table 2-2. Hyamine and TEGO concentration calibrated by SDS

	EP (ml)	Calibrated Concentration (M)
Hyamine	4.10	0.0010
TEGO	4.58	0.0009

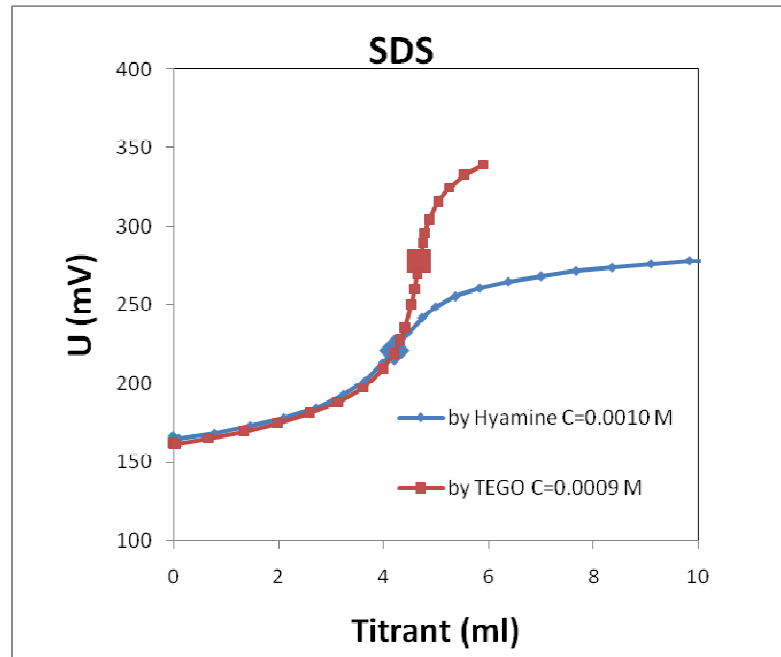


Figure 2-7. titration curves of SDS by hyamine and TEGO

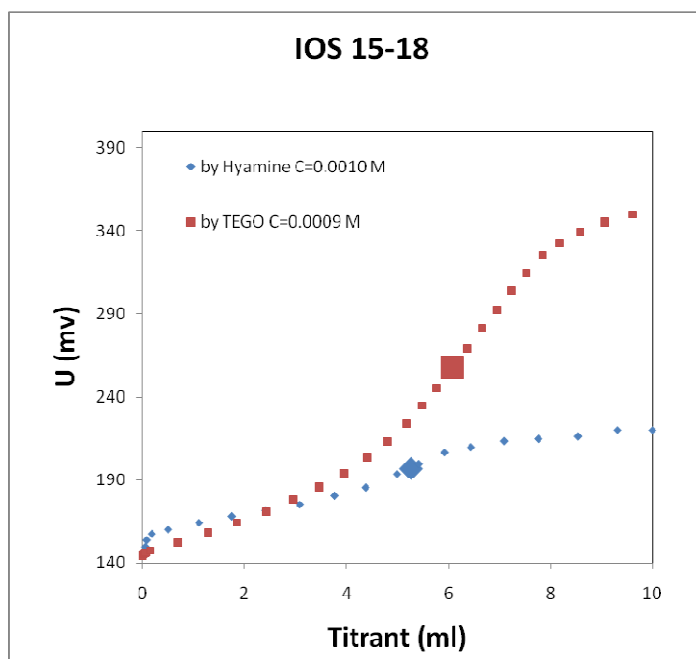


Figure 2-8. titration curves of IOS₁₅₋₁₈ by hyamine and TEGO

Internal olefin sulfonate (IOS₁₅₋₁₈)

The titrations of the IOS₁₅₋₁₈ aqueous solution (2ml) by TEGO and hyamine give the same concentration as shown in Figure 2-8 and Table 2-3, but TEGO gives bigger potential jump around the end point.

C_nO-xylene sulfonate sodium (n= 8, 9, 12 and 24)

Four surfactants, C_nO-xylene sulfonate sodiums (2ml, made at 0.002M), were titrated by hyamine as shown in Figure 2-4. C₁₂OXS and C₂₄OXS give clear end points. The titrations of C₁₂OXS by TEGO (0.0009M) and hyamine (0.0010M) give same and correct concentration and results are plotted in Figure 2-9. When carbon chain becomes shorter, such as n= 8 and 9, no clear end point is present by Hyamine titration, however, titration of C₈OXS by TEGO gives clear and accurate end point shown in Figure 2-10. The details of the parameters are listed in the Table 2-3.

Table 2-3 titration results by Hyamine and TEGO

	EP by hyamine (ml)	Concentration (M) by Hyamine	EP by TEGO (ml)	Concentration (M) by TEGO
IOS ₁₅₋₁₈	5.26	0.0026	6.00	0.0027
C ₁₂ OXS	4.21	0.0021	4.67	0.0021
C ₈ OXS	-	-	4.30	0.0019

Here, we conclude that TEGO is a better titrant compared with Hyamine and will be used for the ionic surfactant titration in the future.

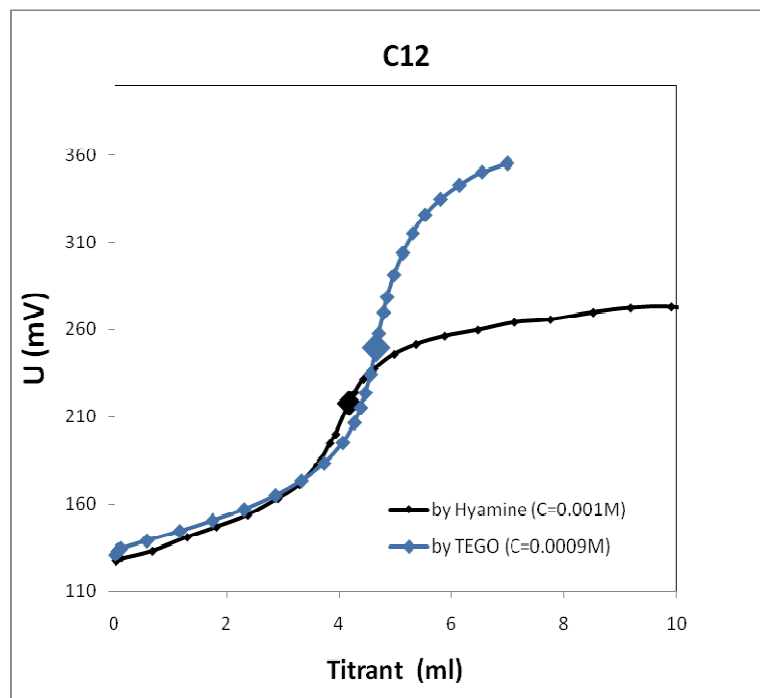


Figure 2-9. titration curves of C₁₂OXS by hyamine and TEGO

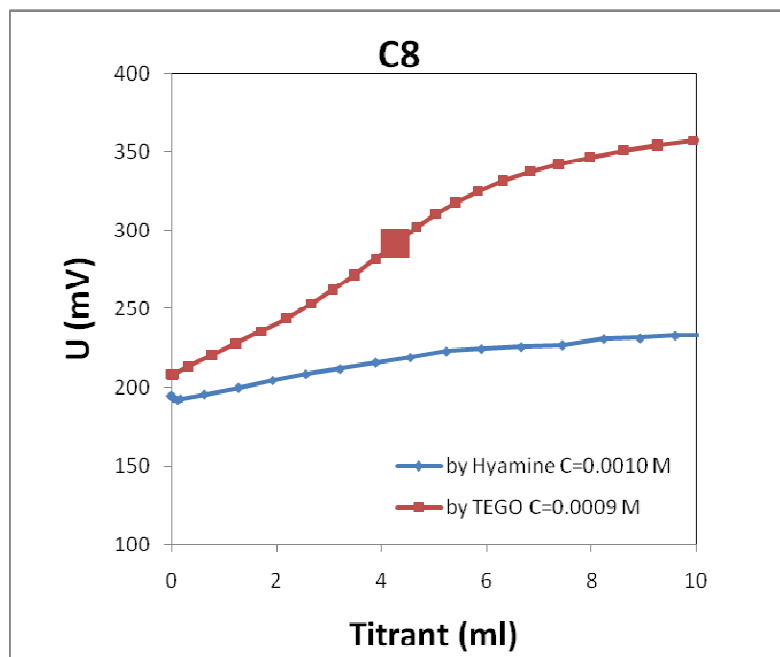


Figure 2-10. titration curves of C₈OXS yamine and TEGO

2.4.4 Effect of Organic Solvents

The electrode used here is not solvent-resistant as its membrane contains PVC.¹ It can be briefly cleansed or rinsed with methanol. The amount of methanol should not exceed 5% for long-term use. Lower alcohols to the extent of 15, 10 and 5% for methanol, ethanol and propanol can be tolerated. Higher concentration, e.g., 30% methanol and 20% ethanol, shorten the electrode life. Higher alcohols (butanol and above) are powerful membrane poisons and should be avoided. Acetone, chloroform, tetrahydrofuran, etc, will become imbibed into the PVC membrane, so should obviously be avoided.³

In addition, the presence of the organic solvent in the surfactant solution affects the titration results. For example, the magnitude of the potential

break is depressed by the presence of water-miscible solvents such as ethanol and propanol as shown in Figure 2-11.⁷ These substances are frequently added to keep relatively hydrophobic materials, such as long-chain soaps in the solution.

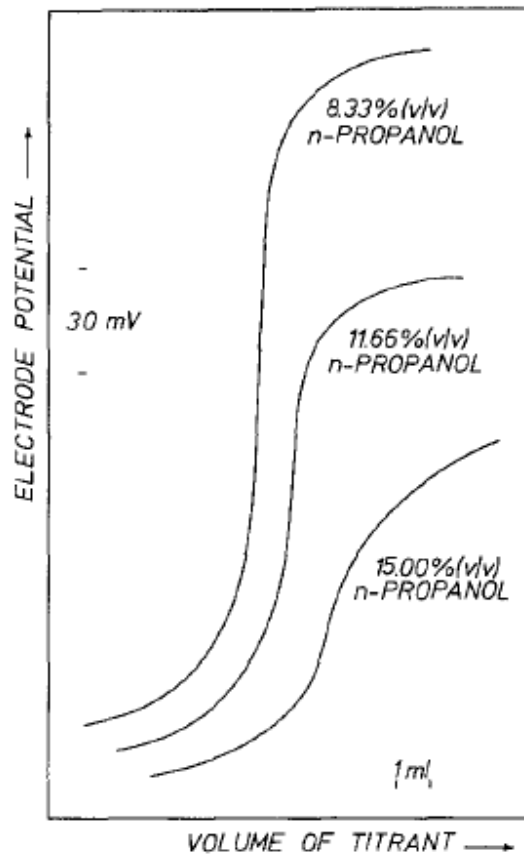


Figure 2-11 Depression of the potential break by addition of alcohols. The effect of propanol on the titration of sodium stearate with 0.004 M cetyltrimethylammonium bromide at pH12. Curves displaced for clarity (adapted from Ref 7)

Also, an alcohol can be partially converted into its alkoxide conjugate base in an aqueous alkaline solution⁸ and gives end point during the titration, An example is shown below: 2.6 g HPLC grade IPA was mixed with 18 g

0.1 M NaOH aqueous solution and diluted to 50ml by DI water. pH of this solution is adjusted to pH 11 by adding 0.1 M NaHCO₃ aqueous solution. When it was tested by hyamine and TEGO, Both show clear end point of IPA as shown in Figure 2-12. Mixture of IPA and Na₂CO₃ also shows clear end point. It was found that the end point is not only affected by the amount of IPA, but also affected by pH and amount of DI water. IPA is an important component in the our current procedure of the soap extraction, However, the titration results of soap extracted by this procedure is not accurate due to the incorporation of IPA. this will be further discussed in the manual of soap extraction.

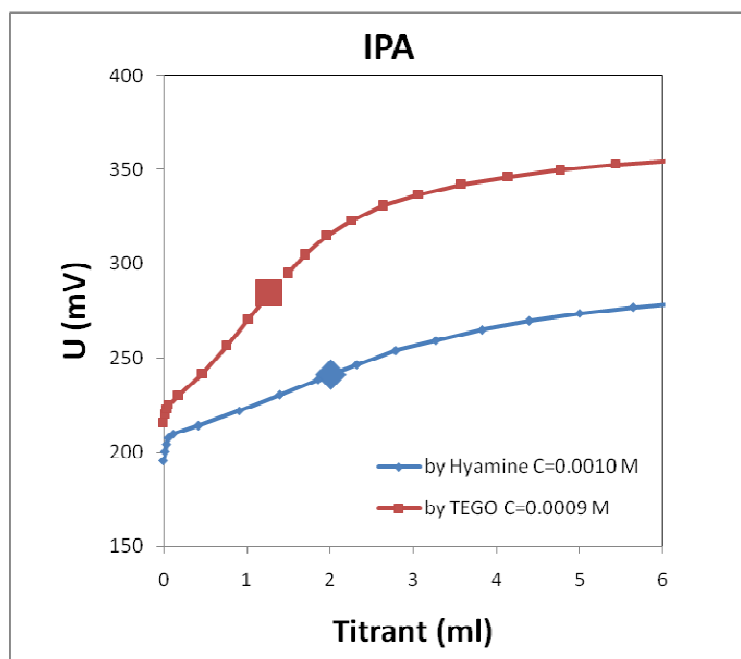
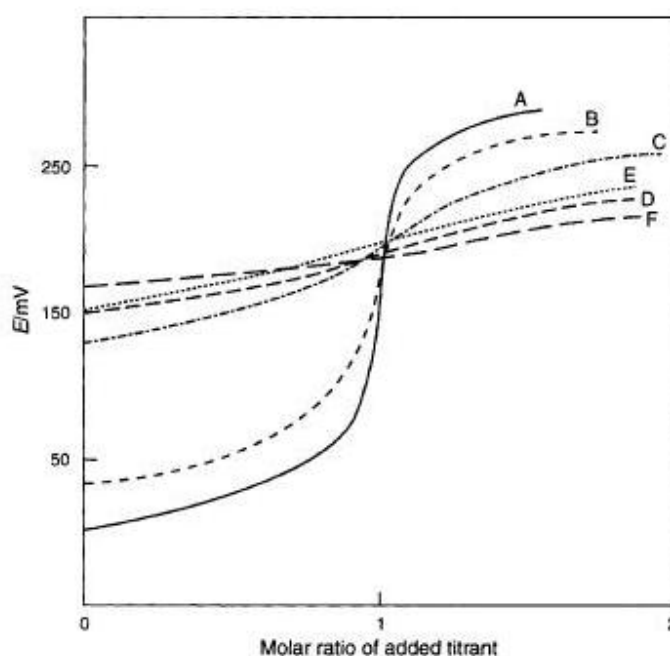


Figure 2-12. titration curve of IPA by hyamine and TEGO

2.4.5 Effect of Sample Size

The electrode shows bigger potential jump when the surfactant becomes more concentrated as shown in Figure 2-13.^{9,10}

Surfactant sample should be diluted within the range of 10^{-2} - 10^{-5} M to get accurate result according to the electrode manual¹ and it is better to keep the concentration between 10^{-4} - 10^{-5} M help preserve electrode life. Also, incorporation of surfactant into micelles reduces its activity, to which the electrode responds and hence the surfactant concentration range 10^{-4} - 10^{-5} M is greatly suggested.



	Surfactant concentration/ mol dm ⁻³	Titrant concentration/ mol dm ⁻³
A	2.5×10^{-5}	4×10^{-3}
B	2.5×10^{-4}	4×10^{-3}
C	4×10^{-5}	1×10^{-3}
D	2.5×10^{-5}	4×10^{-3}
E	2×10^{-5}	1×10^{-3}
F	2×10^{-5}	1×10^{-4}

Figure 2-13. Titration plots at different concentration levels of surfactant and titrant (adapted from Ref 9-10)

2.4.6 Effect of Nonionic Surfactant.

It is suggested by the electrode manual¹ that 1ml 0.1 wt% Triton X-100 should be added into every 50 ml surfactant solution to keep the electrode clean. It is known that the presence of nonionic surfactants influence the formation of micelles,³ hence, the effect of Triton X-100 was studied and the results are shown in Figure 2-14. It was found that the inflection point of SDS becomes ambiguous with increasing volume of 1% Triton X-100 when more than 1ml Triton X-100 was added into 50 ml SDS solution. So 1ml 0.1% Triton X-100 suggested by the electrode manual¹ is low enough to get good titration results.

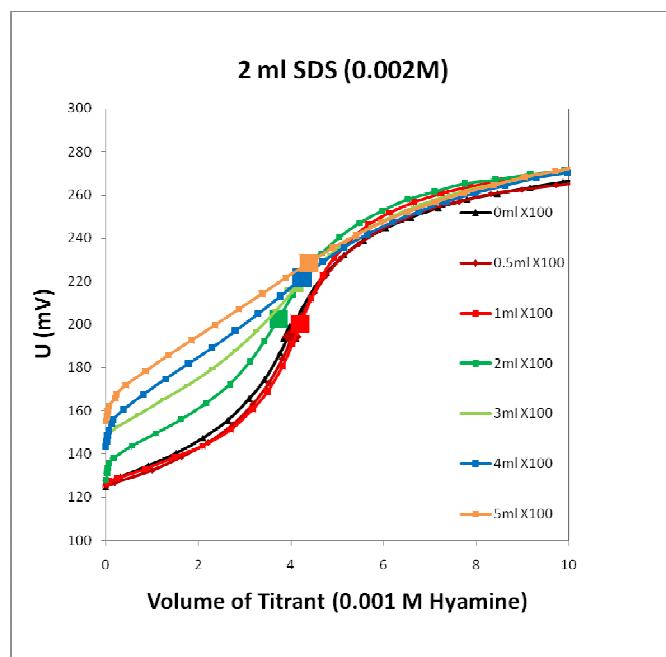


Figure 2-14. Titration curves of SDS by adding different amount of Triton X-100

2.4.7 Titration of Cationic Surfactant

Leyu titrate a cationic surfactant, CTAB, by SDS as the titrant.¹¹ It is important to notice that when the concentration of the cationic surfactant is

very low, the adsorption by the glassware is significant. A plastic vessel should be used or the glassware should be rinsed by the sample before using.

2. 5 Conclusions

A procedure of potentiometric titration was established for measuring ionic surfactant concentrations. The surfactant titration is improved by using TEGO as the titrant instead of Hyamine. Also, a better reconditioning solution, C₁₂-o-xylene sulfonate sodium, is found. Various factors, which affect the titration result, are discussed, such as surfactant chain length, organic solvent, sample size and nonionic surfactant.

2. 6 Reference

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