New Colorimetric Assay Procedure for Polyoxyethylene Non- ionic Surfactants

M. AMINUDDIN[1] AND H.D.C. RAPSON[2]
[1]*Chemistry Department, Islamia University, Bahawalpur, Pakistan,*
[2]*Pharmacy Department, Chelsen College of Science and Technology, Manresa Road, London, SW3, U.K.*

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Summary: A study has been made for colorimetric assay procedure, based on the possibility of a reaction of polyoxyethylene type non-ionic surfactants with acetyl chloride in the presence of ferric chloride to produce a coloured complex.

The various factors such as validity of Beer's law, stability of reagent and the complex and the nature of the complex have been studied.

Introduction

Polyoxyethylene non-ionic surfactants contain a hydrophilic portion which is a polar structure, e.g., -$(CH_2$-CH_2-O-$)_n$, together with a hydrophobic part such as R-C_6H_4O-, where R is alkyl group. It is the extent of hydration of the hydrophilic portion via hydrogen bonding to the ethereal oxygen atoms that decides the over-all solubility of the non-ionic surfantants.

The determination of non-ionic surfactants present in a variety of products as emulsifiers, softeners, or as wettting agents is usually based on ion-exchange methods [1-4], paper chromatography [5-7], thin layer chromatograpy [8-12], circular thin layer chromatography [13], column chromatography [14-16], gas chromatography [17-24], gravimetric [25-26], colorimetric [27-31], volumetric [32-34], high performance liquid chromatography [35- 38], and super critical fluid chromatograpic method [39].

The determination of non-ionic surfactants by colorimetric method usually involves precipitation of the non-ionics, as phosphomolybdate or silicotungstate, followed by dissolution of the precipitate to obtain solution in a suitable form for measuring the absorbances. However, these methods including other techniques mostly depend on separation process and are liable to be tedious, non-reproducible associated with errors of significant magnitude.

The present work is aimed to develop a colorimetric method for non-ionics based on a simple reaction, giving a wine red cololuration to the soluble product, with ferric chloride, dissolved in acetyl chloride. This reaction has been suggested by Waszeciak and Nadeau [40] who used the reaction for identification of products by gas chromatography.

Results and Discussion

In the initial stages of the work, the nature of reaction of the surfactants with acetyl chloride in the presence of ferric chloride was not clear since the product formed only showed absorbance in the case of surfactants being present below 100 ppm. Further investigation led to the conclusion that a certain interval of time was necessary for completion of the reaction.

Calibration Graphs and validity of Beer's Law

When the absorbances of the products are plotted against the surfactant concentrations, straight lines passing through the origin were obtained for both the non-ionics, Lissapol-N and Triton X-100. Fig. 1 and 1(a) showed the absorbance as a function of surfactant concentration. At all concentration levels from 6.0 ppm to 60 ppm a linear relationship was observed.

The values of absorbance for surfactant concentration below 6.0 ppm in case of Lissapol-N seemed not to fit well in the linear relationship curve. This may be that the rate of reaction at lower concentrations is very slow. Table-1 and 2 summarized the values of absorbances of the surfactants of different concentration at different reaction time intervals.

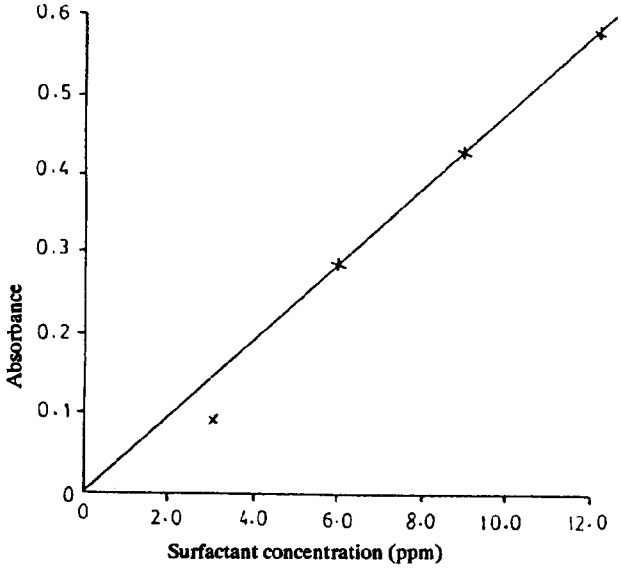


Fig.1: Concentration of Lissapol-N versus absorbance relationship.

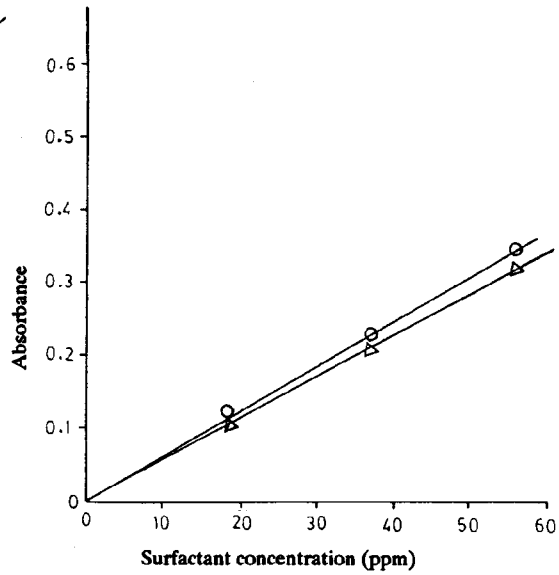


Fig. 1(a): Concentration versus absorbance relationship at different reaction time.
Δ = Triton X-100 (0.5 hr reaction time).
O = Triton X-100 (1 hr reaction time).

Table 1: Effect of time on the complexation reaction of the reagent with non-ionics.

Time Internval (hours)	Absorbances Concentration of Surfactants (Parts per million) Lissapol - N 1.5	3.0	6.0	9.0	12.0
0.5	0.02	0.08	0.28	0.42	0.56
1.0	0.08	0.08	0.29	0.44	0.58
1.5	0.06	0.09	0.29	0.44	0.58
2.0	0.06	0.09	0.29	0.43	0.58
33.0	0.04	0.12	0.25	0.38	0.50

Table 2: Effect of time on the complexation reaction of the reagent with non-ionics.

Time Interval (hours)	Absorbances Concentration Surfactants (Parts per million) Triton X - 100 18.82	37.64	56.46	75.28
0.5	0.11	0.18	0.32	0.25
1.0	0.12	0.23	0.34	0.28
1.5	0.12	0.23	0.34	0.30
2.0	0.11	0.22	0.32	0.30
26.0	0.11	0.24	0.30	0.28
47.0	0.12	0.22	0.29	0.27

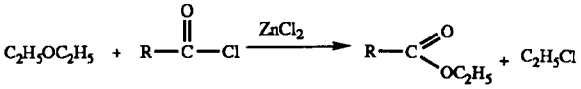
2. Stability of the absorbing species

(a) Effect of time

The complex formation between surfactants and the reagents seemed to be time dependent. It was thus necessary to ascertain the time limits for the equilibrium to be achieved. The results in Table 1 and 2 were used to plot the absornaces of surfactant(s) at a known concentration against time. In the case of Lissapol-N as shown in Fig. 2, it was observed that at all the concentrations (1.5, 3.0, 6.0, 9.0 and 12.0 ppm) the reaction equilibrium was attained just after 30 minutes. Fig. 3 showed a similar behaviour with Triton X-100. The reaction was complete in less than an hour and the product was stable over a long period of time extending upto 2 hours. For Triton X-100 it was also observed that the trend for molecular absorption was decreased with increased concentration of the surfactant (75.28 ppm). This may presumably be due to incomplete reaction following short of the reagent i.e. ferric chloride.

(b) Nature of the product

Polyxyethylene condensate has ether linkages and is expected to give a reaction as presented by Underwood [41] for simple ther:



(R = acetyl)

The identification of the products could be achieved by saponification of the ester or by gas liquid chromatography (GLC). The reaction applied

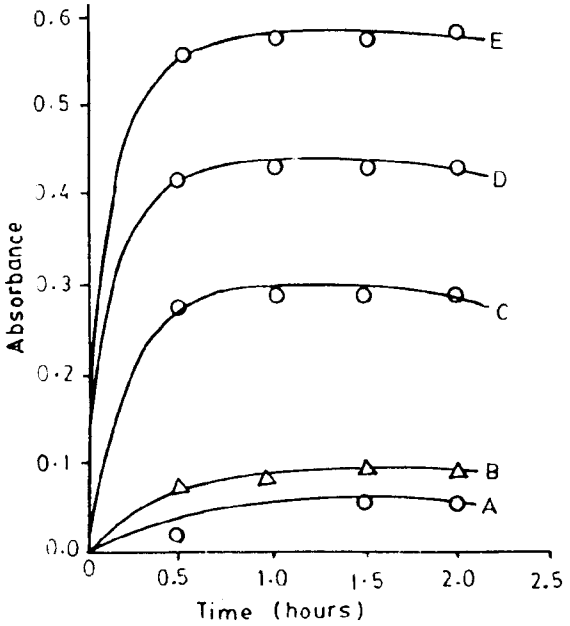


Fig. 2: Reaction time for complexation.
A = Lissapol N in concentration of 1.5 ppm.
B = Lissapol N in concentration of 3.0 ppm.
C = Lissapol N in concentration of 6.0 ppm.
D = Lissapol N in concentration of 9.0 ppm.
E = Lissapol N in concentration of 12.0 ppm.

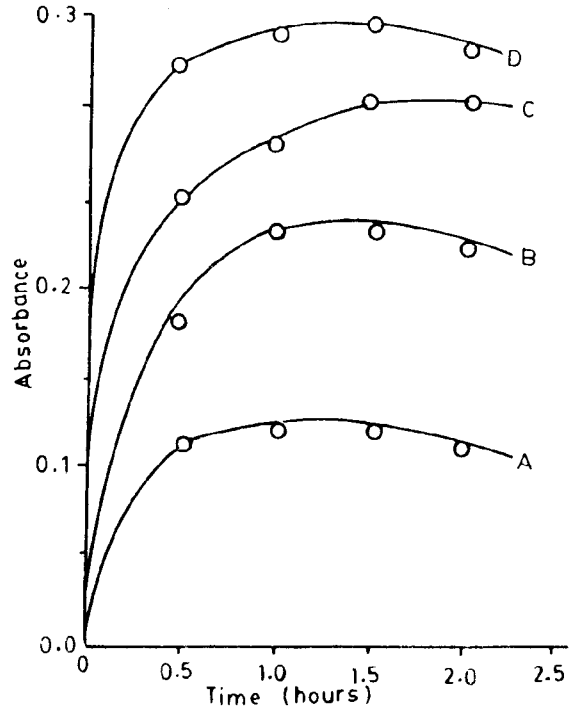
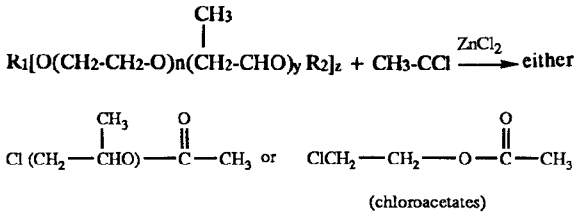


Fig.3: Reaction time for complexation:-
A = Triton X-100 in concentration of 18.82 ppm.
B = Triton X-100 in concentration of 37.64 ppm
C = Triton X-100 in concentration of 75.28 ppm.
D = Triton X-100 in concentration of 56.46 ppm.

to polyethers i.e. polyoxyethylene compounds suggested by Waszeciak and Nadeau [40] would be as follows:



During identification of products by gas chromatography [40], it was found that zinc chloride in place of ferric chloride offered difficulty in the reaction because of being relatively insoluble in the reaction mixture. Ferric chloride on the other hand was soluble in the reaction mixture. Experiments revealed that 1:1:1.2 by weight ratio of polyoxyethylene adduct, acetyl chloride and ferric chloride gave improved experimental conditions. A little larger quantity of ferric chloride was found to give quantitative reaction.

Finally it may be concluded that the reaction product forms a micro environment for radiation absorption at suitable wavelength in conformity with the surfactant's properties to offer micellar stabilized solutions similar to enhancement of phosphosphorescence [42] or oxidation of aromatic compounds.

(c) Determination of wave length of maximum absorption

The absorbance of the complexes with the surfactants, Lissopol-N and Triton X-100, were observed at different time intervals. Molecular absorption spectra have revealed that meausrements of absorbance was maximum at 430 nm and 444 nm respectively. A variation in pH, however, caused a shift in λ_{max} (wave length of maximum absorbance).

(d) Measurement of Absorbances

Measurement of absorbances of the complex at λ_{max} requires a reference blank of the same amount of ferric chlolride in acetyl chloride as in the sample. This will remove the spectral interference from the reagents since its little absornace lies in this region.

Experimental

Materials

(a) Reagents

Anhydrous ferric chloride (Hopkins and Williams Ltd.), acetyl chloride (analytical reagent grade), and chloroform (spectroscopic grade).

(b) Surfactants

Lissapol-N (I.C.I.). This was dried under vacuum at 35-40°C for about 25 hours to a constant weight and stored in a desiccator, contained in a tightly stoppered bottle.

'Triton X-100 (B.D.H.)

Solutions used

1. Ferric Chloride Solution in Acetyl Chloride

0.5% and 1.0% w/v solution of ferric chloride were prepared by dissolving an accurately weighed amount of it in acetyl chloride. Freshly prepared solutions were used for each experiment and the solutions were stored in well stoppered flasks. An interval of 90 minutes was allowed before using this reagent.

2. Lissapol N solution

0.0313g of Lissapol N was dissolved in 25 mls of chloroform. 3 ml of this solution was further diluted to 25 ml with chloroform. This solution contained 0.1502 mg of surfactant per ml.

3. Triton X-100 solution

0.0941g of the surfactant, which is anhydrous, was dissolved in 50 ml of chloroform. The solution contained 1.882 mg of the surfactant per ml.

Apparatus

(i) Hilger UV-spek H700, Manual Spectrophotometer.

(ii) Unicam SP-800 Recording Spectrophotometer.

Both instruments were used for absorbance measurements. Silica optical cells of 1 cm path length were employed.

(iii) A thermostated vacuum oven (Townson and Mercer Ltd.)

Procedure

0.1 to 1.0 ml of Lissapol-N or Triton X-100 were withdrawn by pipette into different 10 ml volumetric flasks. One ml of 1% w/v ferric chloride in acetyl chloride was added to each flask. The solutions were allowed to stand for about 20 minutes at room temperature and then diluted to 10 ml with chloroform. The colour developed by the reaction product was intense yellow. The absorbances were measured at wavelengths of 430 and 444 nm for Lissapol-N and Triton X-100 respectively at d different intervals of time. For the reference, the same quantities of the reagents were used as for the sample and subjected to similar treatment with respect to standing and dilution but without surfactant.

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