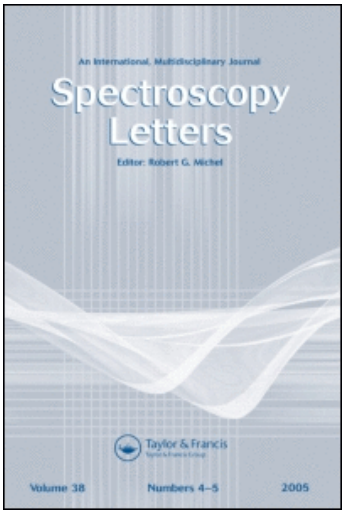

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Determination of some Nonionic Surfactants By Nuclear Magnetic Resonance Spectrometry

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Determination of some Nonionic Surfactants By Nuclear Magnetic Resonance Spectrometry.

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Abstract :

A new, simple and rapid quantitative nuclear magnetic resonance method has been developed for determination of polyoxyethylated nonyl phenol adducts (nonionic surfactants) and their pharmaceutical products. Among other peaks the PMR spectrum of the adduct has a well-defined singlet system (at 3.6 ppm in deutero acetone) which is chosen for quantitative measurements. Maleic acid (δ = 6.3 ppm) is used as a reference standard , and the integral peak area is referred to it. The method gives accurate and reproducible results when applied for the assay of both authentic samples and pharmaceutical preparations. In addition, the PMR spectrum obtained helps in confirming the identity and purity of the adduct.

INTRODUCTION

Polyoxyethylene alkylphenols are useful as active constituent in contraceptive creams causing immobilization of the spermatozoa.

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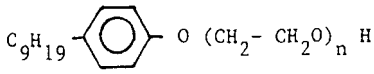
In addition , they act as a unique solubilizing agent for iodine; the combination possessing antibacterial properties and known as iodophor or iodine-tenside complex. Lutensol AP10 and Lutensol AP20 are examples of nonylphenol ethylene oxide tensides , show the structure below:



n = 10 in Lutensol AP10

n = 20 in Lutensol AP20

The reported methods for the estimation of alkylphenol ethylene oxide adducts are either gravimetric[1], volumetric [2,3], colorimetric [4,5], and other spectrophotometric methods including IR procedures[6-8]. In addition to the gas-liquid chromatographic procedures [9,10]. All are non specific and depend upon the ethylene oxide polymer content of the molecule. On the other hand, IZAWA [11]pointed out that the alkylphenol ethylene oxide adducts at λ max at about 277 nm is a linear function of concentration . Also El-khateeb et al [12]described an U.V. spectrophotometric method for the assay of these compounds, making use of the cleavage of their ether linkages by refluxing with hydriodic acid followed by extraction and determination of the liberated alkylphenol by differential Δ-A procedure. Although the method is specific yet it is time consuming similar to many reported methods[13 , 14].

This communication describes a new method, involving the application of PMR spectrometry, for the assay of Lutensol APlo and Lutensol AP20 and their pharmaceutical preparation.

EXPERIMENTAL

A varian T6o-A NMR spectrometer was used throughout the study. The internal standard maleic acid purchased from British Drug Houses, while deuterated acetone (d_6) and tetramethylsilane (TMS) were purchased from Aldrich Chemical Company Inc. (USA). Authentic Lutensol AP1O and Lutensol AP20 were obtained from (BASF AG , Ludwigshafen, W. Germany). While Delfen vaginal cream obtained from ORTHO pharm. Ltd.,Sounderton Buckinghamshire, England .

PROCEDURE

For Authentic Samples :

From a stock solution of alkylphenol adduct in deuterated acetone (d_6) , transfer quantitatively an aliquot quantities in the range of 15-60 mg adduct, in a small glass stoppered test tube. Add 2 ml of maleic acid solution in acetone (d_6) , the concentration of which is 20 mg/ml; stopper the tube and mix well then transfer 0.5 ml of the solution to an NMR tube. Run the PMR spectrum taking care to adjust the spin rate to eliminate side bands as much as possible. Reference all peak field positions to TMS at zero ppm. Measure the integrals of the sharp singlets at about 3.6 and 6.3 ppm , for the adducts and the maleic acid respectively, three times and get the average of each. Calculate the weight of the adduct from the following equation :

$$Wa = \frac{Hs}{Ha} \cdot \frac{Ma}{Ms} \cdot \frac{Ia}{Is} \times Ws$$

Where I = integral of signal (mm)

H = Number of protons within the signal.

M = Molecular weight.

W = Weight (mg).

The subscripts "a" and "S" stand for the adduct and standard maleic acid respectively.

The equation could be written as :

$$Wa = \frac{2 \times 661.4}{20 \times 116.04} \times \frac{Ia}{Is} \times Ws(\text{for Lutensol AP10})$$

and

$$Wa = \frac{2 \times 1101.4}{40 \times 116.4} \times \frac{Ia}{Is} \times Ws \text{ (for Lutensol AP20)}$$

For Selfen Vaginal Cream (ortho) :

It is labelled to contain 5 gm pe cent nonylphenoxy polyethoxy ethanol as active ingredient. Mix the contents of at least three containers and accurately weigh portions of the cream equivalent to 20-50 mg of the adduct, in a glass stoppered test tube . Add 2 ml of the maleic acid solution in acetone (d_6) , the concentration of which is 20mg/ml. Stopper the tube and shake well to affect complet extraction of the adduct . Transfer 0.5 ml of the clear extract to an NMR tube and proceed as previously described.

Results and Discussion :

The proton NMR spectra (60 MHZ) of pure Lutensol Ap10 I and Lutensol AP20 II in acetone (d_6) are shown in figures (1) and (2) respectively. All signals , measured in δ - scale , are referenced

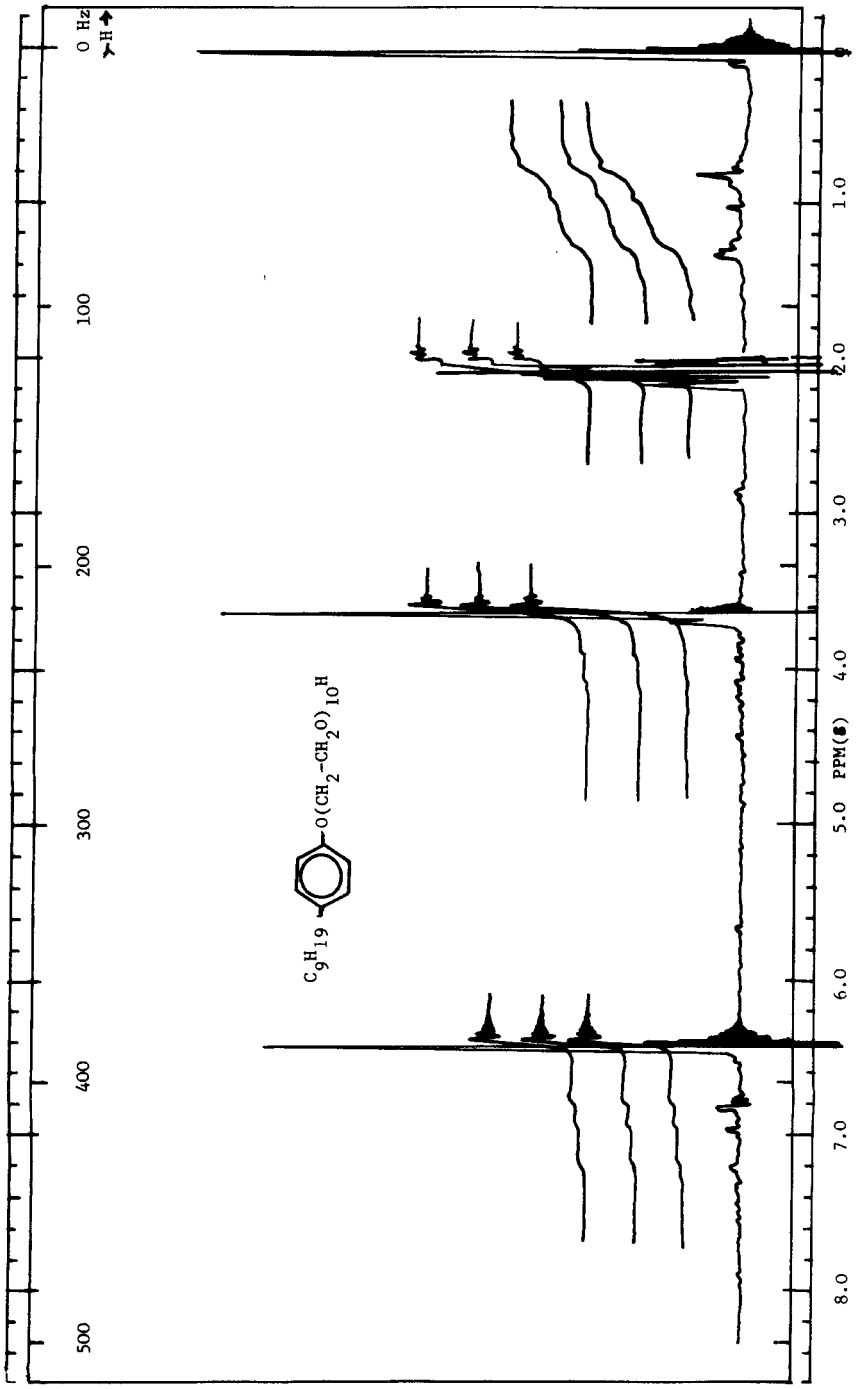


Figure 1 - PMR spectrum of Lutensol AP10 in acetone (d_6) containing maleic acid.

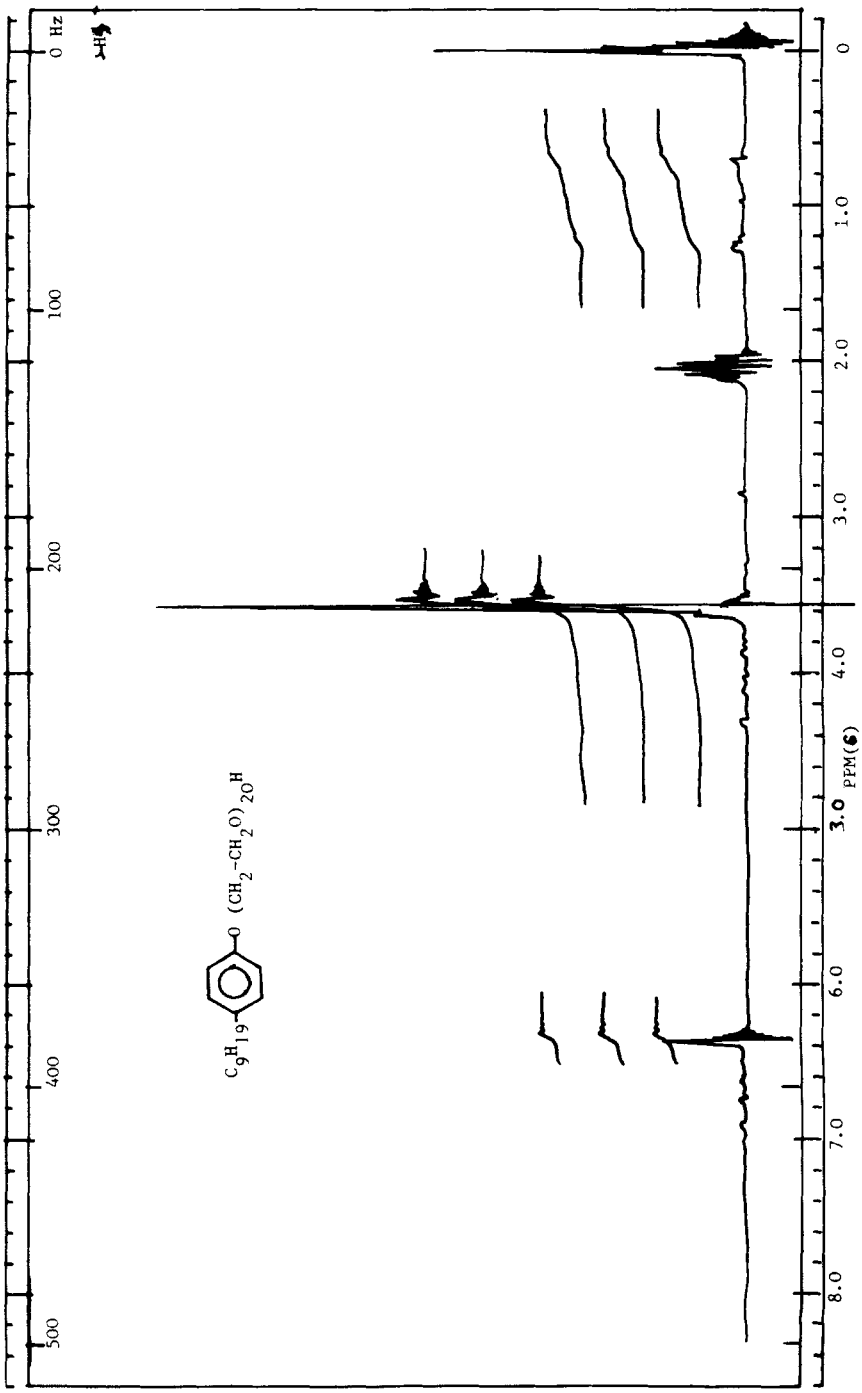


Figure 2 - PMR spectrum of Lutensol AP20 in acetone (d_6) containing maleic acid .

Table I - The percentage Recoveries of Authentic Lutensol AP10

Sample No.	Integral Ratio* Ia/Is	Lutensol AP10 Taken(mg)	Found (mg)	% Recover
1	1.30	15.00	14.81	98.77
2	1.76	20.00	20.11	100.55
3	2.20	25.00	25.07	100.28
4	2.81	32.00	32.05	100.16
5	3.40	40.00	39.25	98.13
6	3.70	42.00	42.17	100.39
7	4.33	50.00	49.38	98.77
8	4.78	55.00	54.54	99.16
9	5.25	60.00	59.83	99.72

Average % Recovery = 99.53 $\pm$ 0.89***

* Average of three measurements.

** The concentration of maleic acid in all solutions is 40 mg.

*** Standard deviation.

to TMS whose singlet is positoned at 0.00 ppm . The spectrum of each adduct is charctrised by a sharp singlet positioned at 3.6 ppm, representing the protons of the equivalent tweenty or fourty protons (in adduct I and II respectively) of the ethylene oxide polymer

Table II - The percentage Tecoveries

of Authentic Lutensol AP20

Sample No	lutegral Ratio* Ia/Is	Lutensol AP20		%Recovery
		Taken(mg)	Found(mg)	
1	2.12	20.00	20.15	100.73
2	2.60	25.00	24.79	99.17
3	3.14	30.00	29.77	99.22
4	3.75	35.00	35.50	101.57
5	4.25	40.00	40.29	100.73
6	5.45	52.00	51.71	99.44
7	5.80	55.00	55.15	100.28
8	6.40	60.00	60.67	101.12

Average % Recovery = 100.28 ± 0.91***

* Average of three measurements.

** The concentration of maleic acid in all solutions is 40 mg.

*** Standard deviation.

content of the molecule. This sharp signal was chosen as analytical peak for the quantitative determination of the adduct by comparing its integral value to that of a known concentration of the internal standard maleic acid (previously recommended [15]. The convenient downfield resonance position (6.3 ppm) of its two equivalent

methylene protons , results in interference-free quantitative analysis. The para substituted aromatic ring shows its charcteristic pattern around 7 ppm , In addition to the multiplet around 1 ppm representing the alkyl group protons, both help in confirming the identity of the adduct but are not suitable for quantitative determination due to their low integral values relative to their high molecular weights.

Tables I and II show the mean percent recoveies obtained when this method is applied for the assay of both Lutensol AP10 and Lutensol AP20 (respectively) . The results demonstrate good precision (average recoveies are 99.53 $\pm$ 0.89 % and 100.28 $\pm$ 0.91 % for Lutensol AP10 and Lutensol AP20 respectively). Figure (3) indicates a linear relationship between the integral ratio (Ia/Is) in milimeters and the concentration of the adducts in miligrams

On the other hand, when the method is applied for the assay of Delfen vaginal cream (ortho) it gives reasonable results with an average recovery of 99.43 $\pm$ 0.53 % as shown in Table III.

Delfen cream is claimed to contain 5% nonylphenol ethylene oxide (Lutensol AP10) together with 0.35% acetic acid, in addition to other unstated amount of propylene glycol, stearic acid, rose essense and parahydroxy benzoic acid.

Figure (4) shows the PMR spectrum of acetone (d_6) extract of Delfen cream , it shows no-interference from other resonance lines corresponding to other ingredients.

The percent recoveries obtained by the proposed PMR method comply with the results obtained by applying the direct U.V. spectrophotometric method [11,12] at λ_{max} 276 nm for both the authentic adduct I (99.96 $\pm$ 0.18 %) and Delfen cream [16] (99.74 $\pm$ 1.98%). However,

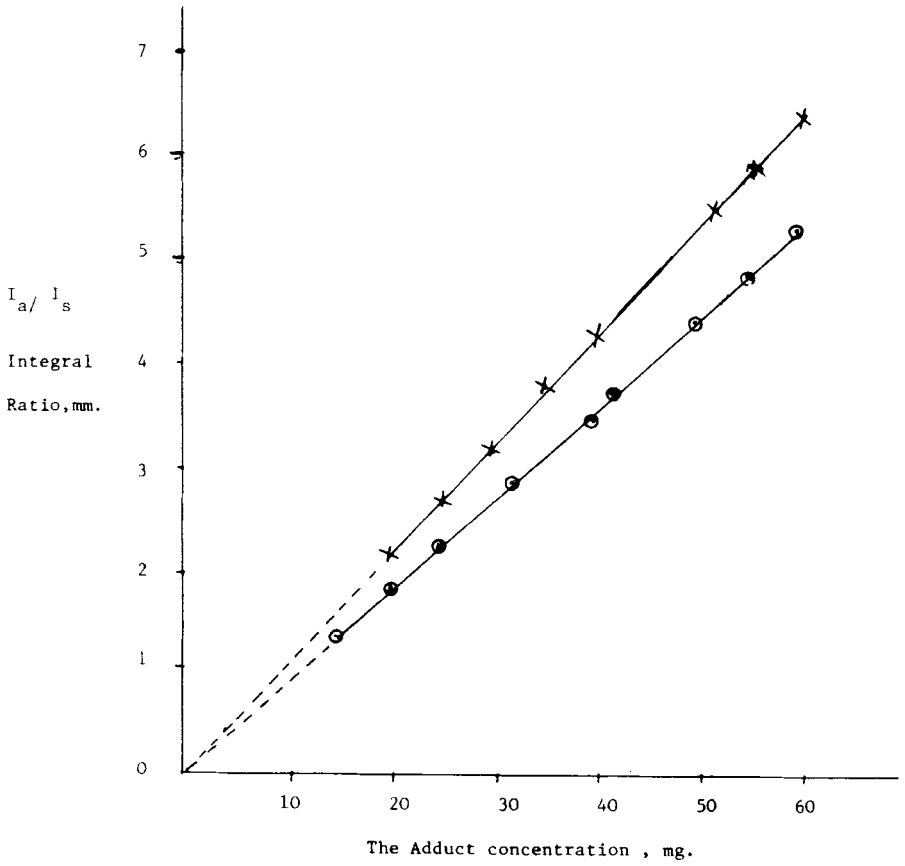


Figure 3 - Calibration Graph of Adducts:

Integral ratio of Lutensol AP10 (●)

Integral ratio of Lutensol AP20 (✖)

Table III - The Percentage Recoveries of

Lutensol APlO in Delfen Cream (ortho)

Sample No	* Integral Ratio	Lutensol APlO		% Recovery
	Ia/Is	Claimed(mg)	Found (mg)	
1	1.75	20.00	19.95	99.75
2	2.20	25.00	25.07	100.28
3	2.60	30.00	29.63	98.77
4	3.05	35.00	43.70	99.14
5	3.48	40.00	39.66	99.15
6	3.94	45.00	44.90	99.78
7	4.35	50.00	49.57	99.14

Average % Recovery = 99.43 $\pm$ 0.53 ***

* Each one gram cream is claimed to contain 50 mg Nonylphenol adduct.

** Average of three measurements.

*** The concentration of maleic acid in all solutions is 40 mg.

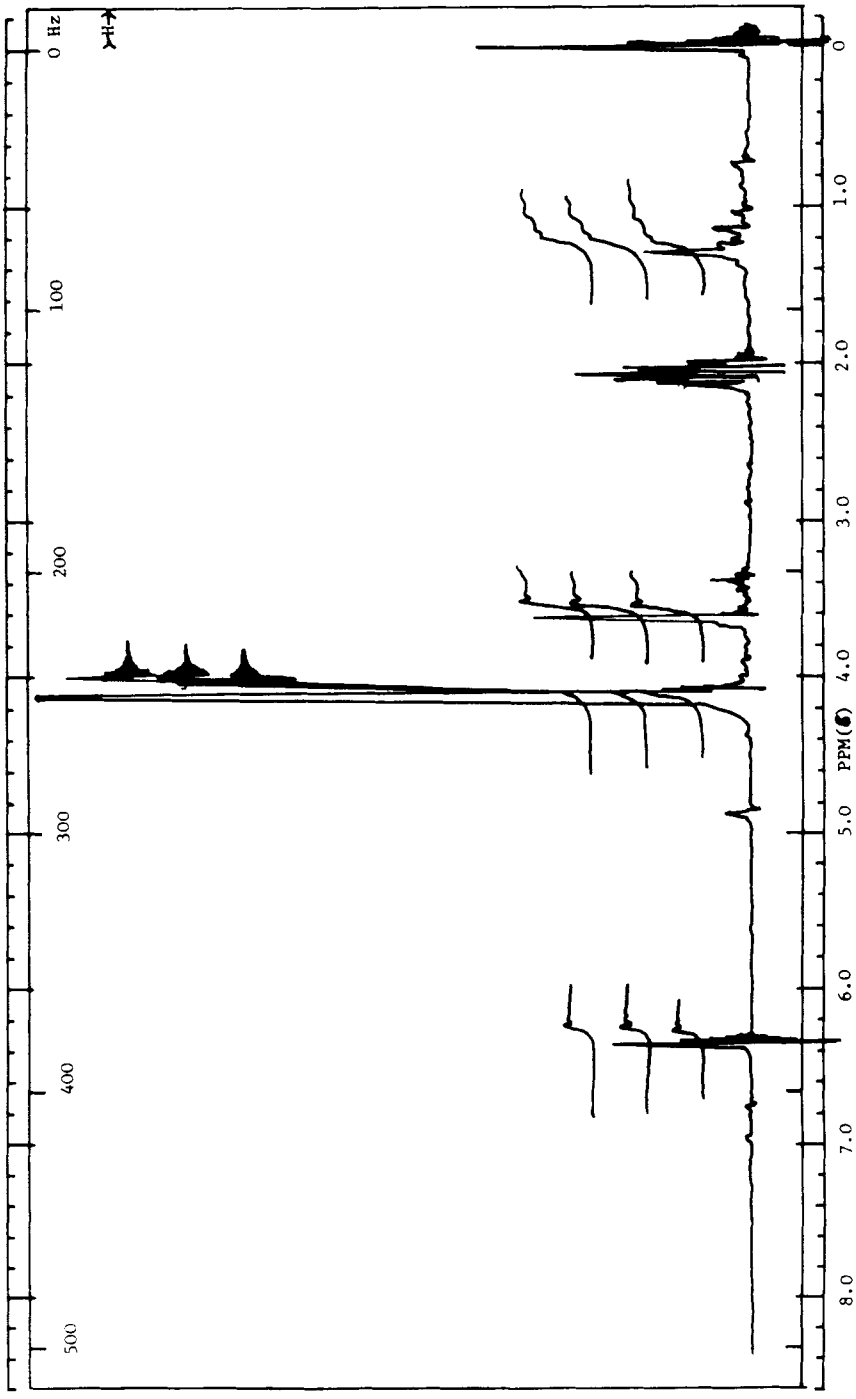


Figure 4 - PMR spectrum of Delfen cream extract in acetone (d_6) containing maleic acid.

it should be pointed out that little informations are mentioned in literatures concerning the analysis of pharmaceutical products and that the method reported[16] before for the analysis of pharmaceutical products necessiate preseparation of nonyl phenol adducts from the other U.V. absorbing ingredients which interfer with the U.V spectrophotometric method.On the contrary, the proposed PMR method is simple, rapid and does not require preseparation of the adduct , since there was no evidence for interference from other ingredients when the method was applied for Delfen vaginal cream.

In addition the method provides the PMR spectrum of the adduct which helps in its identification and checking its purity.

REFERENCES

1 - J. Oliver and C. Preston , Nature, 164 , 242 (1949).

2 - N. Schönfeldt, J. Am. Oil. Chem. Soc.,32 , 77 (1955).

3 - A. Scher,Fette -Seifn-Antrichm., 63 , 617(1961).

4 - J.R. Weber, E.F. Degour and K.S. Bahjat , Anal.Chem., 36,678(1964).

5 - R.G. Stewart,Analyst (london) ,88 , 468 (1963).

6 - C.Glassmann and K. Maennchen, Fette-Seifen Anstrichmittel,65, 741 (1963).

7 - K. Muller and D. Noffz , Tenside,2 , 68 (1965).

8 - C.D. Frazee,Q.W. Osburn and R.O. Crisler,J.Am. Oil Chemist's Soc., 41 , 808 (1964).

9 - M. Panetti and Capella , Chem. Ind. (Milan) 48 (10) , 1071 (1966) (Ital.) . Through C.A., 66 , 12151[a] (1967).

10 - E.W. Neuman and H.G. Nadeau, Anal. Chem. , 35 , 1454 (1963).

11 - Y. Izaw , Yukagaku ,. 11 , 627 (1962).

12 - S. El-Khateeb , S.M.Hassan , A.K.S. Ahmad and M.M. Amer, Tenside Detergents, 16 (1) 27 (1979).

13 - A.Barber, C.C.T. Chinnick and P.A. Lincoln, Analyst , 81 , 18-25 (1956) .

14 - L. Gatewood and H.D. Graham , Anal. Chem. , 33 , 1393 (1961).

15 - S.S.M. Hassan , J.of Association Official Analytical Chemists, 61 , 1 (1978).

16 - S.El-Khateeb, M.M. Amer and A.S. Ahmad , XIV Conf. Pharm. Sci, Cairo Egypt Feb. (1980).

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