Summary

A new volumetric determination of ethylene oxide content in nonionics was established with sodium tetraphenylborate as a titrant using Congo red as an indicator. This method can be applied to nonionics containing more than 10 units of ethylene oxide. A linear relationship between the units of ethylene oxide and the volume of sodium tetraphenylborate was obtained that six units of ethylene oxide combined with one mole of sodium tetraphenylborate. The accuracy of this titration is about ±3%.

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16. Toyozo Uno and Koichiro Miyajima: Determination of Surface-active Agents. VI.*2 On the Composition of Nonionics-Barium-Tetraphenylborate Complex.*3

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In the preceding paper,*2 the titrimetric determination of ethylene oxide content in nonionics using barium chloride, sodium tetraphenylborate (STB) and Congo red was described. Nonionics containing ethylene oxide was reported not to combine with various kinds of precipitating reagents, such as heteropolic acid and barium chloride[1] or potassium bismuth iodide[2] stoichiometrically. Recently, similar results were obtained with polyethyleneglycol-barium-tetraphenylborate complex by Seher.[3] On the other hand, Schönfeldt reported that 6 units of ethylene oxide combined with 1 mole of potassium ferrocyanate.[4] From the titrimetric results,*2 6 moles of ethylene oxide combined with 1 mole of STB. To make clear this relationship between the units of ethylene oxide in nonionics and the precipitating reagent, several methods were examined using ethylene oxide adducts of nonylphenol and it was concluded that 6 units of ethylene oxide combined 1 mole of STB and 0.5 mole of barium in nonionics with 10~40 units of ethylene oxide.

(1) Determination of ethylene oxide contents by Morgan's method.[5] To determine ethylene oxide contents in nonionics used in the previous work,*2 Morgan's method was employed with following modifications: (a) The Kirsten's reagent containing twice volumes of hydriodic acid was used instead of hydriodic acid alone. (b) Nitrogen gas was used instead of carbon dioxide as a carrier gas.

Results of these determination are shown in Table I. Ethylene oxide content (%) agreed with those obtained by calculation based on the hydroxyl values.

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*2 Part V. This Bulletin, **11**, 75 (1963).

*3 This paper was presented at Kinki branch meeting of Pharmaceutical Society of Japan, November, 1961.

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5) P.W. Morgan: Ind. and Eng. Chem., Anal. Ed., **18**, 500 (1946).

Table I. Determination of Ethylene Oxide in Nonionics by Morgan's Method

Compd.	Ethylene oxide in nonionics (%)			
	Calcd.	Found		
		Total	as AgI	as CH_2Br-CH_2Br
NP 10	58.8	56.9	43.7	13.2
NP 20	79.5	81.5	71.6	9.9
NP 30	85.6	83.1	74.2	8.9
NP 40	88.8	87.3	78.8	8.5

(2) Determination of barium and STB by decomposing complex with mercuric chloride (Neu's method)[6]. It was reported by Neu that barium and-STB in a complex at a ratio of 1 to 2 on Tween. In this experiment, nonionics-barium-STB complex was decomposed with mercuric chloride in accordance with the following equation.

$$\text{Adduct}\cdot x\cdot(C_6H_5)_4B\cdot y\cdot Ba+4xHgCl_2+3xH_2O$$
$$=\text{Adduct}+4xC_6H_5HgCl+(4\cdot x-2\cdot y)HCl+xB(OH)_3+yBaCl_2$$

Boric acid derived from STB was titrated with standard sodium hydroxide after the addition of galactose. Barium chloride was converted to barium sulfate which was determined by gravimetry.

Table II. Determination of STB and Barium in Nonionics-Barium-STB Complex by Neu's Method

Compd.	STB in 100 mg. of complex		Barium in 100 mg. of complex	
	Calcd. (mg.)	Found (mg.)	Calcd. (mg.)	Found (mg.)
NP 10	40.8	40.0	8.8	8.8
NP 20	44.1	42.4	9.5	9.1
NP 30	45.5	43.8	9.8	9.4
NP 40	46.3	45.1	10.0	9.7

As shown in Table II, barium and STB combined at a ratio of 1 to 2 into a complex, similary to the case of Tween.

(3) Gravimetric determination of nonionics-barium-STB complex. From the results of the titration, 6 units of ethylene oxide was estimated to combine with 1 mole of STB. According to the results obtained from the decomposition of the complex, barium and STB combined at a ratio of 1 to 2 into a complex. Therefore, it was concluded that 6 units of ethylene oxide combined with 0.5 mole of barium and 1 mole of STB. Consequently, the following formula was derived.

$$\left[\begin{array}{l} R(OCH_2CH_2)_{n/6}(OCH_2CH_2)_{n-n/6}OH \\ \quad\quad | \\ \quad\quad \tfrac{1}{2}Ba \end{array}\right]^{+}\left[(C_6H_5)_4B\right]^{-}_{n/6} \qquad \text{Formula I}$$

As shown in Table III, this formula was also supported by the results of gravimetric determination. In Table III, A is the volume (ml.) of 0.01*M* STB, consumed by the titration of 10 ml. of 0.001 *M* sample solution and A′ is the calculated weight of nonionics-barium-STB complex, derived by substituting A in formula I.

B is a weight of complex precipitated by the addition of an excess of STB (20 ml. of 0.01*M* solution) to 10 ml. of 0.001*M* sample solution. B′ is the weight of potassium tetraphenylborate, precipitated from the filtrate after the complex B was removed. These values are corresponding to the excess of STB. B″ is the calculated volume of STB consumed by the precipitation, which was derived from fromula II. Therefore,

6) R. Neu : Arzneimittel Forsch., **9**, 585 (1959).

Table III. Comparison between Titrimetric and Gravimetric Determination of Nonionics-Barium-STB Complex

Compd.	Titrimetric determination		Gravimetric determination		
	ml. of 0.01*M* STB (A)	mg. of Complex (Calcd.) (A′)	mg. of Complex (Found) (B)	mg. of KTB[a] (B′)	ml. of 0.01*M* STB (Calcd.) (B″)
NP 10	1.7	13.01	14.0	64.0	2.00
NP 12	2.05	15.45	16.7	62.0	2.28
NP 16	2.75	20.70	21.2	61.0	2.98
NP 20	3.30	23.84	23.6	59.1	3.50
NP 30	5.16	36.21	35.9	52.4	5.48
NP 40	6.65	45.89	45.2	47.6	6.90

Formula II : $20-\left(\frac{\text{mg. of KTB}}{358.34}\right)\times 100$

a) KTB : Potassium tetraphenylborate

A correspond to B″, and A′ correspond to B. Good agreement was obtained between each value of the two series.

(4) The properties of nonionics-barium-STB complex. These complexes are white amorphous powders having comparatively clear decomposition points. They are soluble in acetone, slightly soluble in alcohol, and insoluble in water, ether, and chloroform. From these facts, it seems that barium combines with the oxygen of ethylene oxide in a coordinate bond, while barium combines with STB in ionic bond. In the infrared spectrum of these complexes, the band at 1060 cm^{-1} observed in nonionics disappears and a new band appears at 1030 cm^{-1}. However, the assignment of these bands has not been clarified yet.

Experimental

(1) Experiments (I) and (II) were carried out by the methods of Morgan and Neu.

(2) After the addition of 2 ml. of 0.1*M* $BaCl_2$ solution, 10 ml. of a 0.001*M* sample solution was adjusted to pH 3 with HCl, and 20 ml. of 0.01*M* STB solution was added. The precipitates were filtered through sintered glass filter (No. 4), washed with 10 ml. of H_2O, and dried below 50° in a reduced pressure to a constant weight.····B

After an addition of 2~3 drops of *N*$AlCl_3$ solution 20 ml. of 0.02*M* KCl solution were added to the filtrate. The precipitates were filtered with sintered glass filter (No. 4), washed with H_2O and dried for 3 hr. at 120°.····B′

Summary

In the preceding paper, the titrimetry of nonionics was established with both sodium tetraphenylborate and barium chloride. In this work, the composition of the nonionics-barium-tetraphenylborate complex was studied by Morgan's method, Neu's method, and gravimetry. It was found that 6 moles of ethylene oxide combined with 1 mole of tetraphenylborate and 0.5 mole of barium in the complex in 10~40 units ethylene oxide condensates and the titrimetry was applicable to the determination of the ethylene oxide content in nonionics.

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