APPLICATION NOTE

Quantification of Polyoxyethylene (POE) Percentage in Poloxamers via ^{1}H Benchtop qNMR

nanalysis™

Polymers
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Introduction

Poloxamers, commonly referred to by their trade names, Synperonic®, Pluronic®, and Kolliphor®, are ABA-type triblock copolymers composed of A, polyoxyethylene (POE) and B, polyoxypropylene (POP) monomers as shown in **Figure 1**. These polymers have amphiphilic characteristics derived from the hydrophilic monomer A and hydrophobic monomer B, and as a result, are used industrially for their desirable surfactant properties. These attributes allow poloxamers to act as detergents, emulsifiers, foaming agents, dispersants, and coating materials which are used in industries related to cosmetics, personal care, and pharmaceuticals, to name only a few.

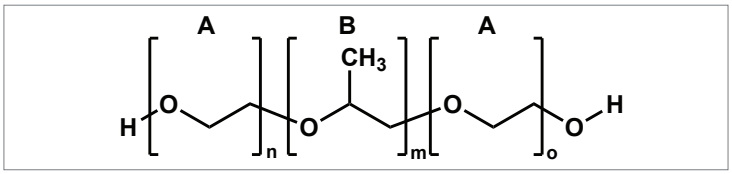

Figure 1: General structure of a poloxamer, which is composed of a central polyoxypropylene block flanked by two polyoxyethylene blocks.

Poloxamers are uniquely identified by the notation, "Pabc", where 'abc' is the poloxamer number. With the poloxamer number, the approximate molar mass of POP and the POE percentage (p-number) in the polymer can be determined. By multiplying the first two digits (ab) by 100, we get the approximate molar mass of POP and by multiplying the last number (c) by 10, we get the approximate POE percentage. For example, P407 is a poloxamer with an approximate POP molar mass of 4000 g/mol and 70% POE content.

Analysis

The POE percentage in poloxamers can be conveniently determined by using ^{1}H NMR spectroscopy. By collecting a 1D spectrum of the polymer sample in a chloroform-*d* solution and integrating *Region 1*, at 1.1 ppm (-CH_3 moieties), and *Region 2*, at 3.5 ppm (-CH_2 and -CH moieties), as shown in **Figure 2**, the POE percentage of the sample can be determined using the equation derived below:

Equation 1

$$wt\%_x = \frac{m_x}{m_x + m_y}$$

Equation 1 represents weight percentage (wt%): where the mass, m, of the sample of interest is divided by the total mass of the sample mixture.

Equation 2

$$n_x = \frac{m_x}{MW_x} = \frac{I_x}{N_x}$$

Here, **Equation 2** defines the correlation between moles of compound, n, relative to the mass, and molecular weight, MW, and how they relate to the integral value, I, obtained from the NMR spectrum and number of protons of interest, N, in the compound.

Equation 3

$$m_{POE} = \frac{I_{POE} * MW_{POE}}{N_{POE}} \text{ and } m_{POP} = \frac{I_{POP} * MW_{POP}}{N_{POP}}$$

By rearranging **Equation 2**, **Equation 3** can be obtained for POE and POP.

Equation 4

$$wt\%_{POE} = \frac{\frac{I_{POE} * MW_{POE}}{N_{POE}}}{\frac{I_{POE} * MW_{POE}}{N_{POE}} + \frac{I_{POP} * MW_{POP}}{N_{POP}}}$$

Equation 4 is obtained by combining **Equation 1** and **Equation 3**.

Equation 5

$$wt\%_{POE} = \frac{\frac{44(I_2 - I_1)}{4}}{\frac{44(I_2 - I_1)}{4} + \frac{58(I_1)}{3}}$$

Fixed variables (MW and N) and manipulated variable (I) are then substituted into **Equation 4**, giving **Equation 5** as shown above, where $I_{POE} = I_2 - I_1$ and $I_{POP} = I_1$. *Regions 1* and *2* represent I_1 and I_2, respectively.

Equation 6

$$wt\%_{POE} = \frac{33(I_2 - I_1)}{33(I_2 - I_1) + 58(I_1)}$$

Finally, **Equation 6** is derived by simplifying **Equation 5**.

The ^{1}H NMR spectrum of Kolliphor P407® showing the relative integrations of *Regions 1* and *2* is displayed in **Figure 2**. The experimental parameters used to acquire the data using the 60PRO are as follows: spectral width: 40 ppm, number of points: 16384, number of scans: 4, scan delay: 5 seconds, spectral center: 10 ppm, pulse angle: 90°, receiver gain: auto. Each sample was run in triplicate to ensure precision.

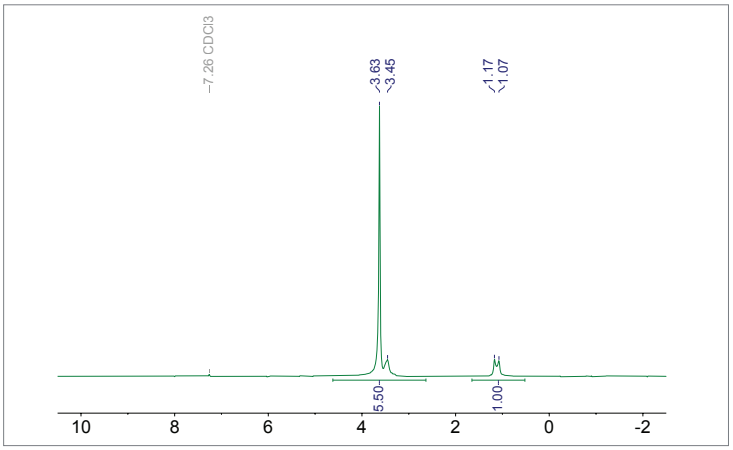

Figure 2: ^{1}H NMR spectrum of Kolliphor 407® in $CDCl_3$, showing the relative integration areas of Regions 1 and 2.

The results acquired using the 60PRO benchtop spectrometer on popular commercial poloxamers are summarized in **Table 1**. The POE percentage was determined from each spectrum, while the average and standard deviation values were determined and compared to the approximate POE percentage obtained from the p-number as well as the values reported by the supplier.

Table 1: POE percentage determined using the Nanalysis™ 60PRO. Values obtained are compared to p-number and POE percentage from the supplier.

Name	Poloxamer Number	POE% (NMR)	POE% (p-number)	%POE (Sigma-Aldrich)
Kolliphor P407®	P407	71.88 ± 0.02	70	71.5 – 74.9
Pluronic F127®	P367	72.46 ± 0.08	70	71.5 – 74.9
Synperonic F108®	P308	80.51 ± 0.05	80	80
Kolliphor P188®	P188	80.92 ± 0.05	80	79.9 – 83.7