Determination of Diester Formation in Diethylene Glycol and Tetraethylene Glycol Monoesters

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ABSTRACT

Polyethylene glycol monoesters on standing rearrange to form diesters. The formation of diester in monoester samples stored at 3 C, 25 C, and 37 C, respectively, for approximately 3 months was determined by reverse phase high performance liquid chromatography (HPLC) in less than one-half hour. Formation of diester increased with increasing storage temperature, regardless of the chemical nature of the monoester substrate.

It has been reported that fatty acid monoesters of polyethylene glycols synthesized either via direct oxyethylation or esterification of the fatty acid with a polyglycol are always contaminated with diester byproducts (1,2). It has been suspected for some time, and recently been reported in this Journal, that monoesters upon standing rearrange to form more diester, and that the presence of diester may have an adverse effect on the wetting ability of monoesters (3). We therefore determined the amount of diester in samples of polyethylene glycol monoesters stored at 3 C, 25 C, 37 C, respectively, for approximately 3 months.

In the past, analysis of monoesters by various extraction techniques was time-consuming and several investigators reported differing mole ratios of free polyglycol, monoester, and diester in the test sample (4,5). We were able to determine the amount of monoester and diester in test samples by reverse phase high performance liquid chromatography (HPLC) in less than one-half hour. The method was similar to that reported for the determination of other surfactants (6). The analytical column used was a μ-Bondapak-C_{18} (Waters Assoc., Milford, Mass.). The mobile phase was 80:20 methanol/water (v/v), and detection was accomplished with a differential refractometer (Waters Assoc., Model R-401).

Samples were synthesized according to a method described by Weil et al. (3). Diester formation was minimized through the use of a large excess of polyglycol. All samples were washed free of catalyst and unreacted polyglycol with water. The water wash did not increase the amount of diester in the sample, due to rearrangement of monoester, as indicated by the data for tetraethylene glycol dilaurate at 0 days (Table I). Formation of diester increased with increasing storage temperature and time, regardless of the chemical nature of th monoester substrate. The precision of the method, expressed as maximum relative deviation, was the greatest deviation from the average peak area for five consecutive injections and was within 0.8 % (Table I).

HPLC analysis offers a rapid method for the determination of diester content of simple homologous monoester samples which have been stored under a variety of conditions.

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TABLE I

Percent Diester in Monoester Samples[a]

	Diethylene glycol monopelargonate[b] at			Tetraethylene glycol monopelargonate at			Tetraethylene glycol monolaurate at		
Days	3 C	25 C	37 C	3 C	25 C	37 C	3 C	25 C	37 C
0		3			5			9[c]	
14	12	14	17	11	15	20	9	9	13
18		13	18		14	25			
25	15	17	18	10	16	26			
28							9	10	19
50	15	17	32	11	21	37			
51							11	13	28
80	15	32	40	13	28	40			
81							9	15	35

[a] % Disester = $\frac{A_d}{A_m + A_d}$ X 100; Where A_m = area monoester, A_d = area diester. Samples were washed free of catalyst and polyethylene glycol with distilled water.

[b] Maximum relative deviation for samples stored for 80 days at 3 C, 25 C, and 37 C was ± 0.8% or less.

[c] Unchanged before and after water wash.

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