

**GLYCOL ESTERS: OPTIMIZATION AND  
EVALUATION OF EMULSIFYING PROPERTIES**

**BY**

A.A.Borayi, N.O.Shaker, F.H.Abdel Salam  
and M.Sadek

Chemistry Department, Faculty of Science,  
Al-Azhar University for Girls,  
Nasr City, Cairo. Egypt.

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**ABSTRACT**

Optimization of the reaction condition for the preparation of glycol monoesters of fatty acids has been studied. Ethylene glycol monoesters of fatty acids were prepared by a direct condensation reaction procedure. Parameters such as temperature period of reaction and the mole ratio of the reactants on the yield of esters were examined. The proportions of ethylene glycol monostearate increased with raising the mole ratio of glycol : fatty acid to 9 : 1. A reaction period of 6 hours was the time required to favour 90% yield of monoesters. The emulsifying properties of monoesters of ethylene and propylene glycols with fatty acids of different chain length and structure were evaluated. The decanoate, oleate and ricinoleate esters of ethylene glycol were to be the most efficient emulsifiers.

### INTRODUCTION

The products of esterification of ethylene and propylene glycols with fatty acids form an important group of cosmetic raw materials. The stearates are the most important and accounted for over  $\frac{1}{2}$  thousand tons of business in U.S. in 1971 and grown to one thousand tons in 1977 (Swern, 1979). These esters function as emulsifiers, opacifying agents, thickening agents, stabilizers in skin creams and lotions, shampoos and conditioners (Hoffmann, 1978)

Particularly, the monostearate is characterized by the ability to produce the desired emulsification stable over a wide temperature range. Meffert (1984) reported that using glycol stearates, the consistency of oil in water (O/W) and water in oil (W/O) emulsions can be influenced and one can vary the consistency of ointments, creams or lotions to be thicker or creamier.

Previous work (Bevan, Malkin and Smith, 1955; Osipow, 1956; Cavasino, 1972) have described different esterification procedures used for the preparation of glycol monoesters of fatty acids. The products were found to contain not only the monoesters but also appreciable amounts of the diester and unreacted glycol as well (Bistline et al., 1969; Osipow and Rosenblatt, 1967).

In an investigation of this reaction in this

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laboratory, we are interested to know the relative amounts of the products obtained under various reaction conditions. Parameters such as temperature and time of the reaction and the mole ratio of the reactants have been examined to optimize reactions and to estimate product composition.

Esterification of ethylene and propylene glycols with fatty acids of varying chain length and structure was accomplished for evaluation of the emulsifying properties of the different esters

#### MATERIALS AND METHODS

Materials :

Fatty acids were purified by standard crystallization methods. Ricinoleic acids was prepared from castor oil by saponification and the liberated mixed acids were acetylated and precipitated as the urea adduct. Acetylated ricinoleic acid was extracted from the filterate and saponified to obtain the free acid ( Kanfobull, 1958).

Epoxystearic acid was prepared by the in situ epoxidation of oleic acid with peracetic acid according to the method adopted by Greenspan and McKerlller (1948).

Methods :

The products of several experiments were analysed in

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terms of some important characteristics from which the various molecular species were computed. The acid, saponification and hydroxyl values were determined according to standard methods of chemical analysis (A.O.C., 1979, A.O.A.C., 1980). The percentage of mono- and diesters of ethylene glycol was calculated from the ester and hydroxyl values according to the relation used by Brandnea and Birkmeiet, 1960.

$$M = \frac{2}{E / H - 1}$$

Where M is the mole ratio of monoester to diester, E and H are the ester and hydroxyl values, respectively of the ester portion.

Interfacial tension ( $\gamma_i$ )

The method described by Jellinek and Anson, 1949 was followed to evaluate the interfacial tension.

Emulsifying power

Since the monoesters of ethylene and propylene glycol were reported to be useful as emulsifiers in food and diverse applications (Marszall, 1982), a simple emulsifying test for emulsifying action was adopted in this work. The glycol ester was dispersed in 15 ml water, mixed with 5 ml of n-heptane in a 25 ml stoppered cylinder. The mixture was subjected to horizontal strokes for 1 hour in a specially

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constructed mechanical skaker. The cylinder is then removed and placed upright. The efficiency of the ester as an emulsifying agent was here expressed in terms of poor, good and excellent if the formed emulsions were stable for not less than 1 , 2 and over 24 hours respectively.

### RESULTS AND DISCUSSION

The product composition obtained at different temperatures and molar ratios of stearic acid and ethylene glycol are represented in tables 1 , 2.

It is seen that the maximum yield (43.5%) of glycol mono-stearate was obtained at 180°C on a 1:1 mole ratio of the reactants. Raising the ratio of ethylene glycol : acid to 5 : 1 , gave yields around 61%. The proportions of mono-esters could be further increased by using higher glycol to acid ratio. The maximum yield (77.8%) was produced by using excess glycol (9:1) at 140°C. However the finished products contained unreacted acid, as manifested in high acid value. Longer reaction periods were required to incorporate much of the remaining acids into the glycol molecules. After 8 hrs up to 90% monoesters and 4.6% diesters were produced (Table 3).

The optimum experimental conditions which may be followed for the preparation of high yields of monoglycol esters was established in this work. High monoester-containing

products are desirable since the actual functional emulsifier used in food systems and other industries is only the mono-ester portion of the mixture (VanHaften, 1979).

In the second stage of this work, the production of a number of fatty acid esters has been stimulated within conditions of the esterification as just recommended. Homologous even carbon carboxylic acids from decanoic to stearic, unsaturated oleic and linoleic, hydroxy acid ricinoleic and epoxystearic acids were reacted with each ethylene and propylene glycols. Glycol monoesters of a commercial sample of soapstock fatty acids was also included and represent a sample of mixed fatty acids which may be obtained from relatively cheap sources.

The surface activity of the glycol esters was greatly manifested in their efficiency of lowering the interfacial tension between water and paraffin oil from its original value (45 dynes/cm to much lower values ( 12.6 - 22.2), (Table 4 ).

Since several long chain monoesters of ethylene and propylene glycol have been found to be useful as dispersants or emulsifiers in diverse applications (Moilliet, Collie and Black, 1961), a simple test for emulsifying action was used to evaluate the different esters. The evaluation of these esters as emulsifying agents is

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represented in Table 4 .

All the esters were found to affect emulsification under the experimental conditions. The decanoate, Oleate and ricinoleate esters of ethylene glycol were the most efficient emulsifiers with respect to stabilities of the formed emulsions. Esters of propylene glycol were less effective, they might be considered as poor emulsifiers. The presence of double bond or hydroxyl group in the lipophilic part of the C<sub>18</sub> acids were found to have great bearing on the emulsifying property and stability of emulsions.

Similar results have been offered by Bhattacharyya et al, 1984, in their studies with polyethylene glycol esters of fatty acids.

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**Table (I)**  
**Esterification of Ethylene Glycol with**  
**Stearic Acid**

Temp (°C)	A.V.	S.V.	OH value	Mole ratio of Mono/diester	Monoester %	Diester %
80	123.1	168.5	25.1	2.4	22.0	26.5
100	121.1	173.1	29.3	2.6	23.2	16.3
120	102.5	174.5	52.2	5.3	36.3	12.5
140	82.4	193.3	75.1	4.3	36.0	22.9
160	64.2	197.8	78.6	2.9	41.2	26.7
180	53.9	199.8	83.2	2.6	43.5	29.6

Mole ratio = 1:1

Time of reaction : 1 hr.

Table (2)  
Esterification of Ethylene Glycol with Stearic Acid

Temp. (°C)	A.V.	S.V.	OH value	Mole ratio of Mono/diester	Monoester %	Diester %
Mole ratio 5:1						
80	73.5	174.5	75.4	6.0	48.7	14.6
100	66.1	184.2	95.5	8.6	55.4	11.5
120	56.1	196.7	117.6	10.5	61.3	10.6
140	47.8	201.0	120.2	7.4	61.2	14.9
Mole ratio 7:1						
80	71.9	176.6	90.1	12.5	55.9	8.2
100	62.9	190.4	111.1	14.2	61.7	7.8
120	50.3	199.8	139.7	28.5	70.4	4.5
140	41.6	198.5	138.6	15.3	70.8	8.4
Mole ratio 9:1						
80	56.6	179.2	113.0	23.5	66.5	5.2
100	54.0	190.0	125.8	24.3	67.9	5.1
120	47.8	202.8	145.2	33.3	72.1	4.0
140	35.2	198.9	153.6	30.7	77.8	4.6
Mole ratio 10:1						
80	72.4	181.6	100.0	21.9	58.9	4.8
100	58.8	189.7	120.0	22.7	65.4	5.2
120	49.1	192.0	133.2	27.7	70.8	4.6
140	34.1	196.5	151.0	27.0	77.7	5.2

Time of reaction : 1 hr.

Table (3)

Effect of Reaction Period on Esterification of  
Ethylene Glycol with Stearic Acid.

Time	A.V.	S.V.	OH value	Mole ratio of Mono/diester	Monoester %	Diester %
1	47.8	202.8	145.2	33.3	72.1	4.0
2	28.0	217.9	180.2	37.7	81.9	4.0
4	15.2	214.0	189.3	39.2	88.3	4.1
6	11.2	210.5	190.2	42.5	90.5	3.9
8	10.5	218.5	196.7	35.7	90.1	4.6

Mole ratio : 9:1  
Temperature : 140°C .

**Table (4)**  
**Interfacial and Emulsification Properties of**  
**Ethylene (E.G.) and Propylene Glycol (P.G.) Esters**

Esters of	E.G. Esters		P.G. Esters	
	$\gamma_1$ (dynes/cm)	Emulsifi- cation	$\gamma_1$ (dynes/cm)	Emulsi- fication
Decanoic	12.6	Excellent	18.1	Good
Lauric	20.1	Poor	22.2	Poor
Myristic	19.0	Poor	20.5	Poor
Palmitic	18.0	Poor	20.1	Poor
Stearic	18.5	Good	20.0	Poor
Monoepoxystearic	20.5	Poor	23.5	Poor
Oleic	18.8	Excellent	16.5	Poor
Linoleic	18.8	Poor	18.9	Poor
Ricinoleic	18.7	Excellent	16.5	Poor
Soap stock F.A.	18.9	Poor	15.9	Poor

## أسترات الجليكول : تحضيرها وتقييم خواصها كمستحلبات

عفاف أحمد برعى ، نهال عمر شاكر

فاطمه حسنى عبد السلام و محمد صادق

قسم الكيمياء ، كلية العلوم

كلية البنات - جامعة الأزهر - مدينة نصر - مصر

يتناول البحث دراسة أفضل الظروف العملية اللازمة لتحضير الأسترات الأحادية للأحماض الدهنية مع الجليكولات عن طريق الأسترة المباشره . لذلك فقد أجرى اختبار تأثير بعض العوامل مثل درجة الحرارة وزمن التفاعل والنسبة المولية للمواد المتفاعلة على كمية الناتج من الأسترات الأحادية . ووجد أن نسب احادى ستيرات الجليكول تزيد برفع النسبة المولية للجليكول الى الحامض الدهنى الى ٩ : ١ . وأن اجراء التفاعل لمدة ٦ ساعات يعطى حوالى ٩٠% من الأسترات الأحادية ، وقد تم تقييم الأحماض الدهنية المختلفة مع كل من جليكول الاثين والبرولين كمواد استحلاب حيث وجد أن كل من استرات أحماض الديكانويك ، الأوليك والزيسينوليك لجليكول الاثيلين أكثر قدره على تكوين المستحلبات.