J. Soc. Cosmet. Chem., 26, 523-530 (November 1975)

Some Properties of Ethoxylated Lanolin Derivatives and Their Effect on Cosmetic Application

JUSTIN P. McCARTHY, B.S., and MITCHELL L. SCHLOSSMAN, B.S.*

Presented May 10, 1974, Seminar, Chicago, Illinois

Synopsis—The modification of selected LANOLIN ALCOHOLS with ETHYLENE OXIDE has produced many water and ALCOHOL SOLUBLE DERIVATIVES. Studies of some chemical and physical properties of these functional LANOLIN DERIVATIVES are presented. Physico-chemical measurements of critical micelle concentration (cmc), specific gravity, and viscosity (to the limit of their water solubility) of these derivatives are compared and discussed. The application of these materials in the solubilization of a selected group of perfume compounds is observed. A controlled experiment demonstrating the use of ETHOXYLATES in adjusting the viscosity of a cosmetic gel shampoo is illustrated. References relating to pigment dispersions, solubilization of elected bacteriostats, and other phenomena are briefly reviewed. Some new data in these areas are given.

Introduction

The reaction of lanolin and lanolin alcohols with ethylene oxide produces water-soluble surface-active agents. It is known that the properties of these condensates vary with the length of their ethylene oxide chain. In general, as the ethylene oxide chain increases, the resultant product becomes more surface-active. By varying the aforementioned hydrophobe-hydrophile balance, these derivatives have been known to display unusual properties and functions. In this paper, we will chemically describe these ethoxylates and discuss some of their properties. Specifically, such phenomena as critical micelle concentration (cmc), specific gravity, and viscosity will be highlighted. Studies on solubilization and viscosity control involving these ethoxylates in cosmetic applications will be illustrated.

*Malmstrom Chemical Corp., Linden, N.J. 07036.

Experimental

A. The cmc was determined by the surface tension method (1) using distilled water as a solvent. Concentrations of 1 per cent and less of PEG-75 Lanolin,* PEG-75 Lanolin Oil, PEG-75 Lanolin Wax, Laneth-10 Acetate, Laneth-16, PEG-24 Hydrogenated Lanolin, and Laneth-40, were prepared and the resultant solutions allowed to come to ambient temperature (23/25°C). A DuNuoy tensiometer† was employed and surface tension measurements were made. An average of three dial readings were taken to calculate surface tensions of each of the various solutions. Surface tension is reported in terms of dynes per centimeter. The surface tension of distilled water at ambient temperature was used as the calibration standard to calibrate the instrument prior to determining the surface tension of each of the unknown solutions. The cmc is that concentration range at which a sudden change in surface tension measurement occurs.

B. Specific gravities of all the ethoxylates evaluated were determined using the precision specific gravity chain balance.‡ The instrument was first calibrated using distilled water. The glass cylinder was then dried and charged with the ethoxylate solution and placed in a 25°C water bath for 2 hours. The plummet was then submerged so that it could swing freely in the cylinder without touching the sides. The instrument was then adjusted so that it was balanced; at which time the specific gravity could be read directly.

C. Viscosity determinations to the limit of water solubility were done on a Brookfield Rotational viscometer. Model LVT.δ Two spindles were used; numbers 1 and 2, both for standardizing the instrument and for the samples. The instrument was operated at 30 rpm for standardization and at 60 rpm for the various concentrations of surfactant.

D. The solubilization of perfume compounds study was initiated by our laboratories and prepared by International Flavors and Fragrances, Inc. (I.F.F.).** All tests were conducted in a 20:80 specially distilled alcohol (SDA) 40 ethanol/water medium using a 2 per cent fragrance level. Four ethoxylated lanolin derivatives were used as solubilizers at concentrations of 4 and 8, respectively. These were: (W) PEG-75 Lanolin oil; (X) Laneth-10 Acetate; (Y) Laneth-16; and (Z) PEG-75 Lanolin.

Five popular perfume types were evaluated. They are described by I.F.F. as type A—aldehyde ester; type B—aldehyde ester musk; type C—alcohol al-

---

*Ethoxylan 100, Lantrol AWS, Lanfrax WS55, Ethoxyol AC, Ethoxyol 16R, Ethoxyol 24, and Ethoxyol 40; Malmstrom Chemical Corp., Linden, N.J. 07036.

†Fisher Scientific Co., Inc., 711 Forbes Ave., Pittsburgh, Pa. 15219.

‡Henry Troemner, Inc., Philadelphia, Pa. 19142.

δBrookfield Engineering Labs, 240 Cushing St., Stockton, Ma. 02072.

**521 West 57th St., New York, N.Y. 10019.

Table I
Clear Gel Shampoo

	W/W%
Cocamide	10.00
TEA Lauryl Sulfate	50.00
Linoleamide DEA	5.00
EDTA	0.50
Methylparaben	0.20
Deionized Water	34.30
	100.00

dehyde; type D—terpenes, esters, and resins; and type E—ester, alcohol terpene.

The solutions were prepared at room temperature by first blending the fragrance into the solubilizer and adding this to the water/alcohol mixture with agitation. (The Laneth-16 and PEG-75 Lanolin were heated slightly to convert them to liquids.) This resulted in 40 solutions, which were tested for stability at room temperature and 105°F for a period of 1 month.

E. Viscosity study on a gel shampoo—the following ethyoxylates were tested at 1, 5, 10, and 20 per cent levels in a gel shampoo: (1) PEG-75 Lanolin Oil; (2) PEG-75 Lanolin; (3) Laneth-40; (4) Laneth-16; (5) PEG-24 Hydrogenated Lanolin; (6) PEG-75 Lanolin Wax; (7) Laneth-5;* and (8) Laneth-10 Acetate.

In preparing the gel shampoo, all of the ingredients in Table I were charged in order and heated with mixing to 75°C. The shampoo was then cooled slowly to 55°C. The gel formed was further cooled slowly to 30°C. In the experimental shampoos prepared with the ethoxylates, an equivalent amount of deionized water was removed from the formula. All the raw materials used were taken from the same batch in order to minimize any slight differences found in their analytical specifications. Viscosities were taken initially and then weekly for 2 months. Records of specific gravity and stability were made during this period.

Discussion of results

Saad and Shay (2) described cmc as that point or range at which the constitution of the surfactant solute changes from a disperse state to an equilibrium between molecules (or ions) and aggregates (micelles). It has been noted that properties such as surface tension show an abrupt change at the cmc. Table II illustrates this change. For example, one notices a decreasing

*Ethoxyol 5; Malmstrom Chemical Corp., Linden, N.J.

Table II
CMC Determination Using Surface Tension Data

	Surface Tension (dyn/cm)						
Concentration (% Wt)	PEG-75 Lanolin Wax	PEG-75 Lanolin Oil	PEG-75 Lanolin	Laneth-16	PEG-24 Hydrogenated Lanolin	Laneth-40	Laneth-10 Acetate
0.025	52	—	69	65	—	68	48
0.05	49	59	66	62	58	65	48
0.10	48	58	65	60	55	63	43
0.15	45	57	63	59	54	63	42
0.20	44	58	61	58	57	65	40
0.25	44	59	63	59	57	67	40
0.50	47	59	67	60	59	69	38
1.00	50	59	68	60	59	69	40
cmc (% Wt)	0.20%	0.15%	0.20%	0.20%	0.15%	0.10%	0.20%

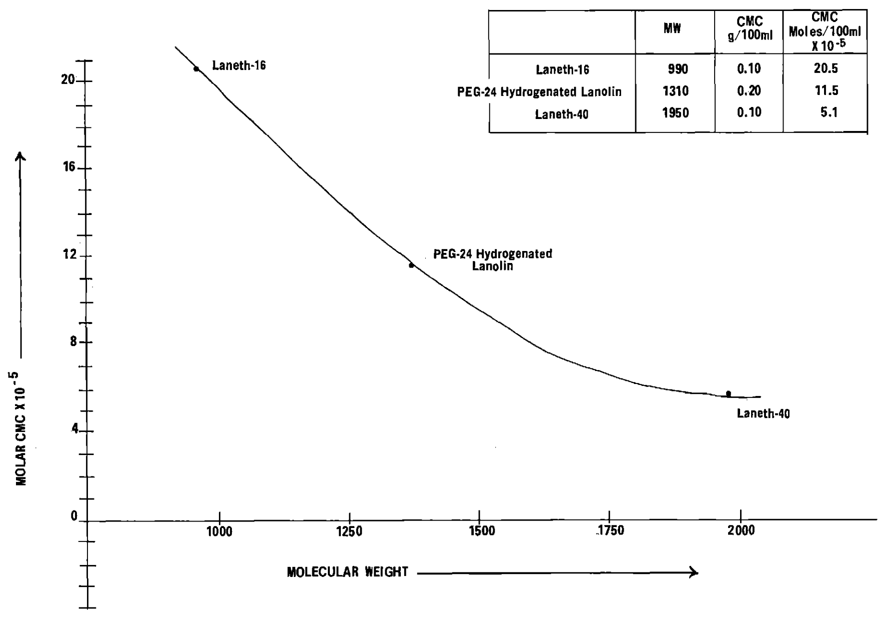

Figure 1. Molar cmc versus molecular weight

trend in the surface tension as the concentration of Laneth-16 increases up to 0.20 per cent. Then the surface tension suddenly increases as the concentration is further increased. The point at which this change takes place is noted as the cmc and is so designated on the bottom line of the table. Furthermore,

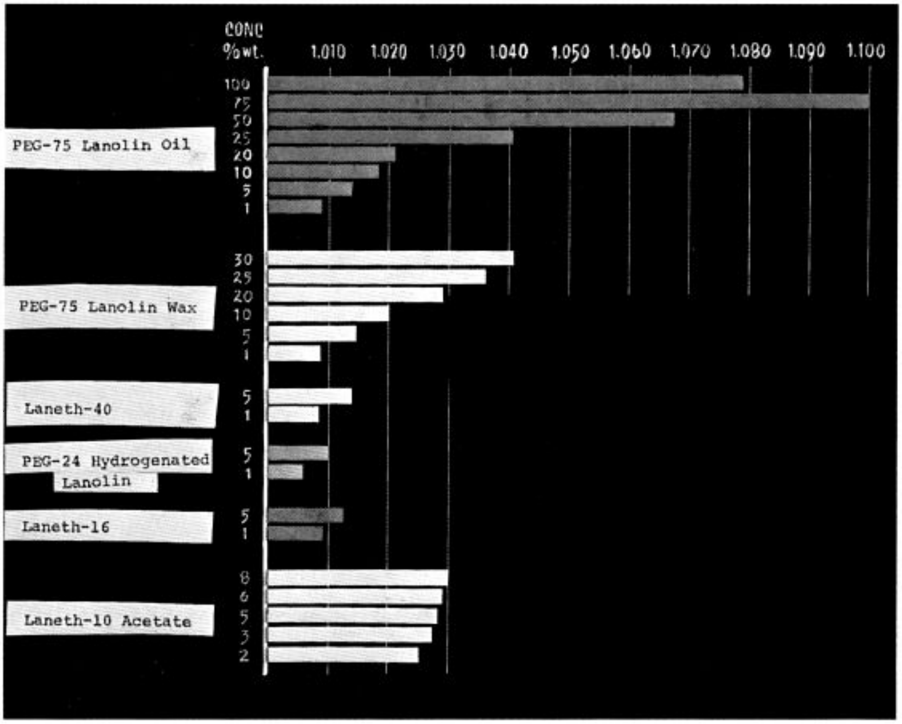

Figure 2. Specific gravity of lanolin ethoxylates in aqueous solutions

on analysis of the results, as the molecular weight of the derivative increases, the cmc decreased as shown in Figure 1, for the lanolin alcohols. In general, we feel that with more accurate methods of cmc determination being available, they might be used to obtain a more accurate picture of lanolin ethoxylates than the surface tension method presented at this time. In the future, comparisons of methods will be evaluated.

Figure 2 and Table III illustrate that both specific gravity and viscosity increased as the concentration of ethoxylates in water increased. The exception to the rule was found with the PEG-75 Lanolin oil solutions. A mamimum viscosity was obtained at a 50 per cent concentration. Specific gravity values did not follow the expected norm, but showed a maximum value at a concentration of about 75 per cent. From the data, it is evident that very slight changes in specific gravity and viscosity were seen within the range of concentrations use. Further increases in the concentration were not possible because the solubility of most of the lanolin ethoxylates in water at 25°C is limited to 5 to 10 per cent. In many cases, at higher levels, the insoluble portions floated to the surface, and the lower portion remained a clear gel. It

Table III
Log Viscosity (CPS) of Ethoxylate Solutions to the Limit of Solubility in Water at 68°F

Product	Concentration Wt %	Log Viscosity (CPS)
PEG-75 Lanolin Oil	100	3.20
	75	3.75
	50	4.18
	25	3.19
	20	1.00
	10	0.93
	5	0.63
	1	0.54
PEG-75 Lanolin Wax	45	5.91
	40	5.41
	35	5.34
	30	3.99
	25	2.57
	20	1.79
	10	0.90
	5	0.70
	1	0.54
Laneth-40	5	0.60
	1	0.54
PEG-24 Hydrogenated Lanolin	5	0.60
	1	0.54
Laneth-16	5	0.54
	1	0.48
Laneth-10 Acetate	8	0.88
	6	0.88
	5	0.80
	3	0.80
	2	0.70

should be further noted that the low range of viscosity values determined are borderline accuracies per sensitivity of the Brookfield viscometer.

The perfume solubilization study demonstrated, that in most cases, the higher level of lanolin ethoxylates produced more significant results. In Table IV, it is shown that Laneth-16 appears to be the most effective solubilizer for these systems. The lanolin alcohol derivatives show superiority to the lanolin ethoxylates as solubilizers. In most cases, there was greater solubility demonstrated at elevated temperatures (105°F). The solubilized perfume compounds that were evaluated indicated good fragrance qualities. These finished products all demonstrated an emollient "after-feel" to the skin. Finally, it

Table IV
Perfume Solubilization Using Lanolin Ethoxylates in a 20% SDA-40 Ethanol/80% Water Medium at 68°F[a]

Perfume Type	Concentration % Wt	PEG-75 Lanolin Oil	PEG-75 Lanolin	Laneth-16	Laneth-10 Acetate
A	4	D	D	D	I
	8	D	D	C	I
B	4	D	D	D	I
	8	D	D	C	I
C	4	I	D	I	I
	8	D	D	C	C
D	4	I	D	D	I
	8	I	D	I	C
E	4	D	D	D	I
	8	D	D	D	D

[a]C = clear solution, (best); D = dispersible, milky solution, (in between); I = insoluble (two distinct phases), (worse).

should be recognized that fragrance compounds of this type and quality are usually prepared in cologne bases containing 75 to 85 per cent alcohol and not vice versa as was done in this experiment. Most likely, many more of the samples prepared would have produced a clear product if just chilled, then filtered. The purpose of this study was to place emphasis on the solubilizing power of the lanolin ethoxylates under the poorest possible condition of relatively high fragrance levels and low alcohol content.

In formulating a gel shampoo, one must consider its viscosity stability. Often times, gel shampoo viscosities increase or decrease rapidly to a point where they are no longer usable. The gel shampoo control used in this experiment (Table I) showed a rapidly decreasing viscosity over the 2-month study. The ethoxylated lanolin and lanolin alcohol additives in most cases stabilized the gel shampoo viscosity after its initial decrease. In every case, except when the PEG-24 Hydrogenated Lanolin and the Laneth-16 were added, the viscosity of the solid gel changed to a free-flowing gel or a liquid with increased concentrations. These exceptions produced increases in viscosity. Laneth-16 produced a very viscous thermally stable gel having good viscosity stability. The PEG-24 Hydrogenated Lanolin showed poor thermal stability. It appears that in most cases, 5 or 10 per cent ethoxylate levels produced the greatest viscosity stability during the test period with correspondingly acceptable thermal stability. Laneth-10 Acetate demonstrated poor stability at 68°F with a sudden decrease in viscosity when 20 per cent was used as an additive.

Additionally, new data on the pigment wetting performance of lanolin ethoxylates will be the subject of a future investigation. Preliminary studies indicate that the PEG-75 Lanolin oil may be a superior dispersing agent for inorganic pigments, especially iron oxides.

A study presented in 1964 demonstrated that lanolin derived solubilizers are effective in solubilizing water insoluble bateriostats in soap and detergent solutions (3). Some newer bacteriostats, not presented in that study, were evaluated using the Laneth-16 derivative as the solubilizer. The results were comparable to the 1964 study.

Summary

Various properties of lanolin ethoxylates have been presented in this paper, and it is quite evident that these properties lend to their marked versatility in cosmetic applications.

Illustrations involving the perfume solubilization power of ethoxylated lanolin derivatives under extremely unfavorable conditions were given. Also demonstrated here was the viscosity control of an anionic gel shampoo system using these ethoxylates.

In conclusion, we hope that we have demonstrated how these multifunctional lanolin ethoxylates may be effectively utilized in future cosmetic developments.

Acknowledgments

The authors are indebted to Dr. Harold Silverman and his staff at the Massachusetts College of Pharmacy for their cmc and specific gravity determinations and the cosmetic research staff at International Flavors and Fragrances, Inc., for their cooperation in the perfume compound solubilization studies. (Received August 13, 1974)

References

(1) P. Becher, *Emulsions: Theory and Practice,* Vol. 1, Reinhold Publishing Corp., New York, 1957, Pp. 34–8.
(2) H. Y. Saad and E. G. Shay, Application of physical chemistry in product development, *J. Soc. Cosmet. Chem.,* **23,** 899–911 (1972).
(3) K. L. Russell and S. G. Hoch, Water-insoluble bacteriostats solubilized in soap and detergent solutions, *J. Soc. Cosmet. Chem.,* **16,** 169–84 (1965).