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SOME PROPERTIES OF AN ETHOXYLATED CASTOR OIL AND ETHOXYLATED OLEYL ALCOHOL

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ABSTRACT

Ethoxylated derivates have been used as surfactants for some years. In this work, ethoxylated castor oil and ethoxylated oleyl alcohol alone and/or their I:I mixtures were used as surfactants in oil/water type of emulsion systems.

The physicochemical properties of ethoxylated castor oil (Simulsol OL 50) and ethoxylated oleyl alcohol (Simulsol 98) have been investigated.

Both of these materials have properties associated with non-ionic surfactants, although considerably soluble in water, the compounds have slight solubility in nonpolar solvents.

Surface tensions of aqueous solutions were measured over a temperature range of 20° to 40°C. CMC were determined by surface

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tension measurements. pH, refractive index, conductivity and density of the two surfactants were also determined.

INTRODUCTION

In this work, some physical and chemical properties of ethoxylated castor oil and ethoxylated oleyl alcohol were investigated.

The two ethoxylated surfactants are both nonionic and are completely miscible with water. In addition they are useful as detergents and emulsifiers in pharmaceutical and cosmetic industry.

The two emulsifiers alone and/or their 1:1 mixtures were used as surfactants in oil/water type of emulsion systems.

EXPERIMENTAL

Materials- Water was deionized and distilled in glass vessels and had a surface tension of 72.6 mNm^{-1} at 20°C (7).

Buffer Solutions, 0.05 M Borate, 0.05 M Phthalate and 0.05 M Phosphate Buffers were prepared according to the Merck Index.

Ethoxylated Caster Oil (Simulsol OL-50) (Seppic-France) was used as received. It was a monionic emulsifier derived from ethoxylation of a triglyceride of vegetable origin (Castor oil). It was substantially homogeneous, amber colour liquid, readily miscible with water. Its HLB value is 13. Its viscosity at 20°C is 450 cps and has a melting point of about 10°C (3,5).

The material corresponds to a structure:

$$\text{Castor oil} - (O{-}CH_2{-}CH_2)_{40}$$

Ethoxylated Oleyl Alcohol (Simulsol 98),(Seppic France) was used as received. It was a nonionic emulsifier based on an ethoxylated fatty alcohol. It was a soft yellow wax with slight characteristic odour, which is readily miscible with water. Its HLB value is 16.5. Simulsol 98 has a melting point of about 37°C(3,5).

The material corresponds to a structure:

Oleyl alcohol-$(O\text{-}CH_2\text{-}CH_2)_{20}$

<u>Methods</u> - Surface Tension : Surface Tensiometer (Model 20-Fischer, U.S.A.) was used to measure the surface tensions of the aqueous surfactant solutions. The instrument was calibrated as indicated in its catalogue and with water at 20°C. A jacketed glass disc connected to a thermostated water bath and equal solution volumes were used. The mean of six measurements were taken. Measurements were carried out at, 20,25,30 and 40°C.

pH was determined using pH meter (Model 12-Corning, U.S.A.). The results were the mean of five determinations.

Conductivity was determined by Conductivity Bridge (Model 31-YSI, U.S.A.). The results were the mean of three readings.

Refractive indices were determined with an Abbé refractometer (Model G and B Carl Zeiss Jena, D.D.R.); and the mean of three determinations were taken.

Different concentrations (% w/w) of the mixtures of surfactants and water, aqueous buffer solutions and oil in tightly covered glass tubes which were equilibrated at 25°C and shaken for 24 hours, at 125 strokes per minute by laboratory shaker (Type L88 1-Gerhardt, Germany) for solubility studies. The limit of solubility was indicated by turbidity of the solutions in the tubes.

Densities were determined by 10 ml pycnometers at 25°C. The results were the mean of five determinations.

Ultraviolet Spectra was taken by double-beam U.V. spectrophotometer over 340-200 nm (model DB-GT-Beckman, U.S.A.).

Infra-Red Spectra was taken by Grating I.R. Spectroscopy over 4000-250 cm^{-1} (Model 457-Perkin Elmer, U.S.A.).

RESULTS

pH of aqueous solutions of the two surfactants were around 5.9-6.0 over the concentration range of 0.0005-1.0 (w/v). The pH was not changed with increased concentration, only a slight inflection point coincident with the critical micelle concentration (CMC) is reached for only Simulsol OL-50.

The refractive indices of the two surfactants over a concentration range of 0.0005-1.0 % (w/v) have not shown any inflection and remained almost constant. The conductance of Simulsol OL-50 started decreasing in value around the CMC and increased further after the CMC point. Whereas, Simulsol 98 remained constant.

The curve of surface tension versus log C, where C is the surfactant concentration, in aqueous and buffer solutions, is linear within a certain concentration range, above which the surface tension remains nearly constant as the concentration is increased. The concentration at which the two linear portions of the curve intersect (Figures 1,2,3,4) was considered to represent the CMC value.

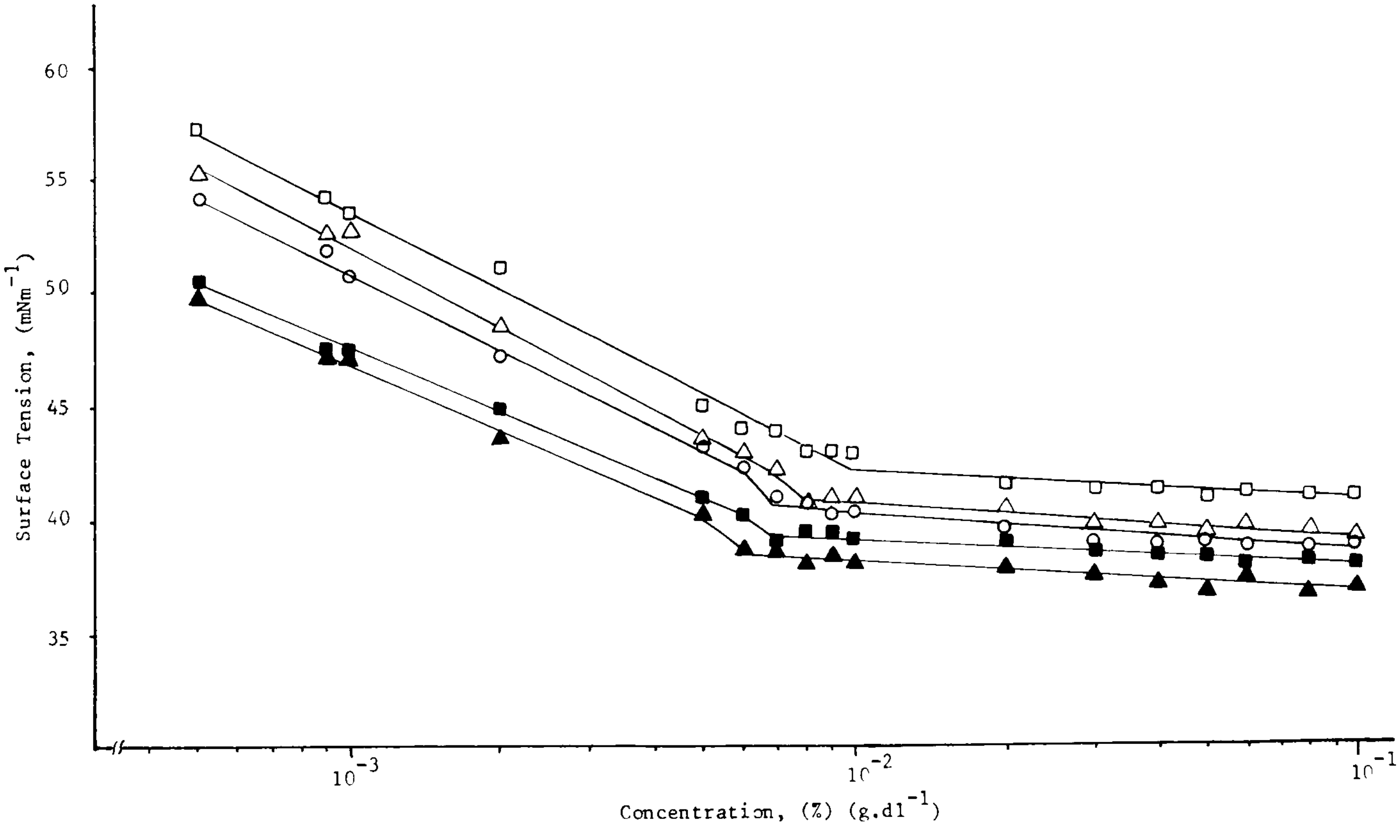

FIGURE 1
The surface tension of aqueous solutions of Simulsol OL 50 at different temperatures.

□ 20°C △ 25°C ○ 30°C ■ 37°C ▲ 40°C

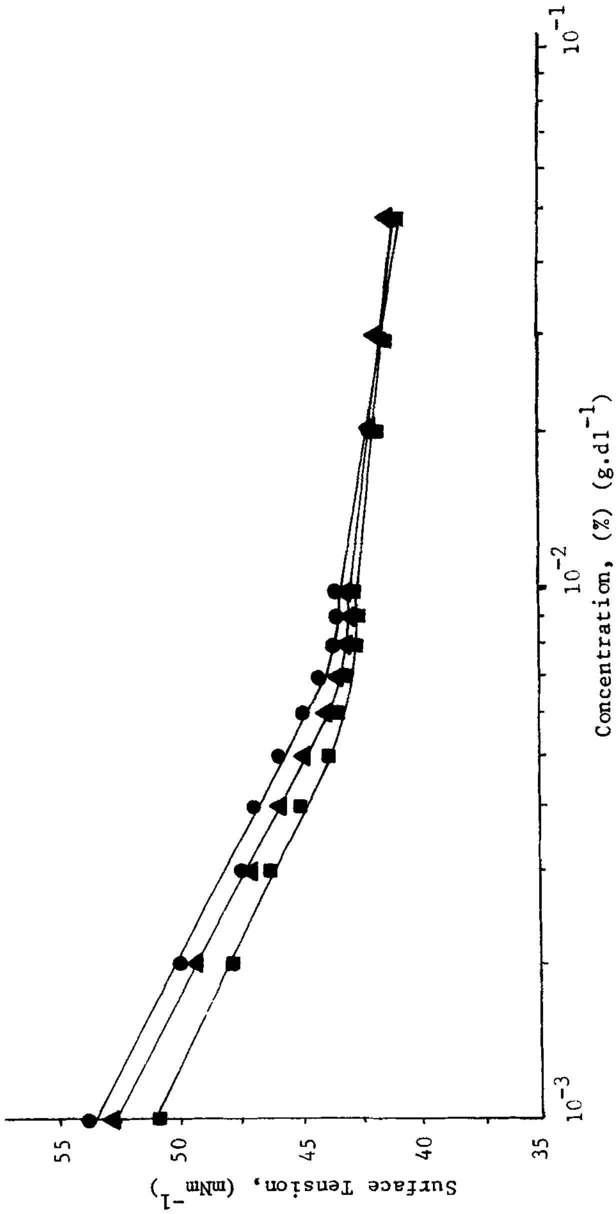

FIGURE 2

The surface tension of solutions of Simulsol OL 50 in aqueous buffer solutions (0.05 M) at 20°C.

- ● Borate Buffer, pH 9.20
- ■ Phosphate Buffer, pH 6.8
- ▲ Phthalate Buffer, pH 4.00

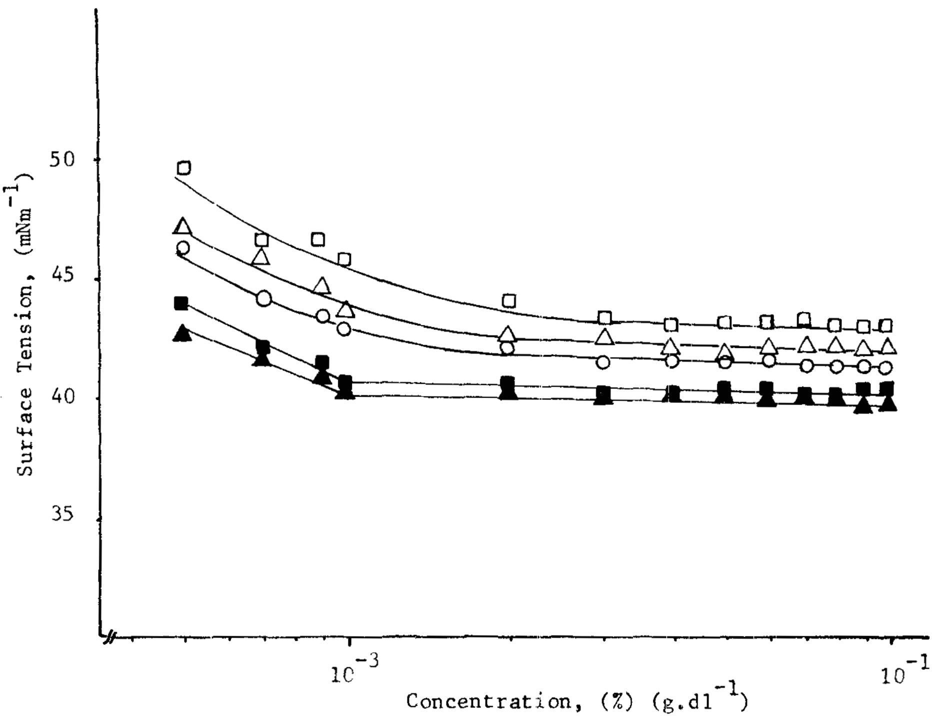

FIGURE 3

The surface tension of aqueous solutions of Simulsol 98 at different temperatures.

□ 20°C
△ 25°C
○ 30°C
■ 37°C
▲ 40°C

The CMC in water was determined at different temperatures 20,25,30,37 and 40°C (Figures 1,2). The effect of temperature on CMC of both of the surfactants are shown in Figures 1,3,5. Measurements of the surface tension in the presence of 0.05 M buffers at 20°C showed that the CMC was reduced when compared with the un-

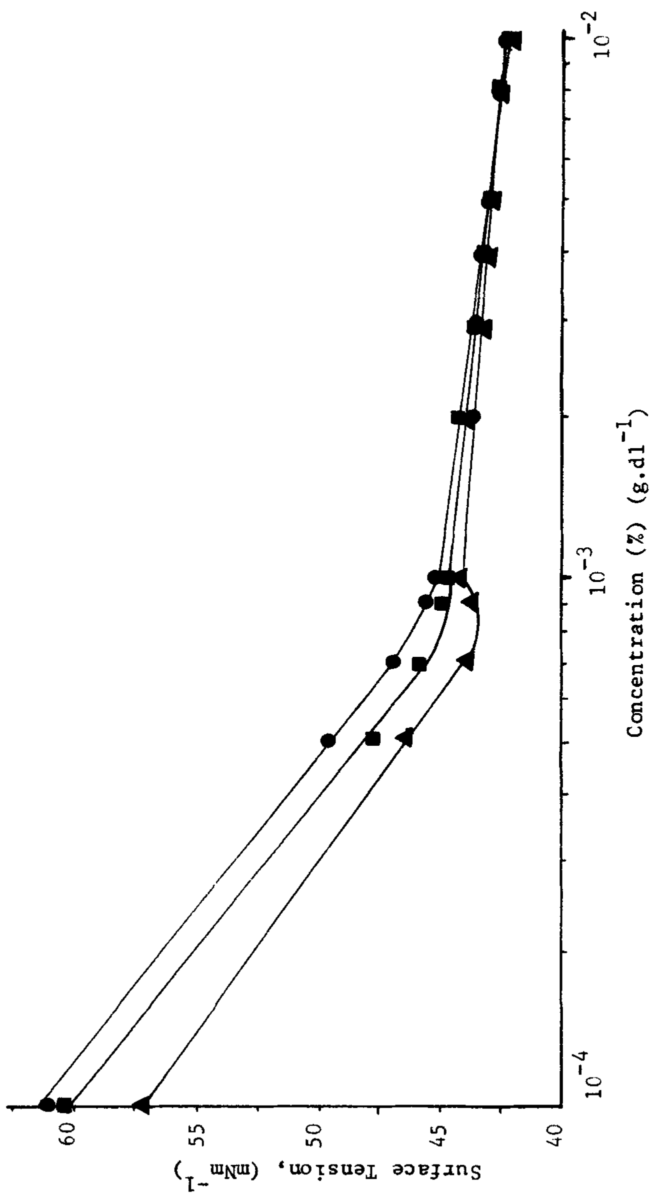

FIGURE 4

The surface tension of Simulsol 98 in aqueous buffer solutions (0.05 M) at 20^{o}C.

● Borate Buffer, pH 9.20
■ Phosphate Buffer, pH 6.80
▲ Phthalate Buffer, pH 4.00

TABLE 1

CRITICAL MICELLE CONCENTRATION OF SIMULSOL OL - 50
IN AQUEOUS SOLUTIONS AND AT DIFFERENT pH'S OF VARIOUS TEMPERATURES

Temp °C	CMC ($g \cdot dl^{-1}$) (Water) x 10^3	CMC ($g \cdot dl^{-1}$) (pH 9.2) x 10^3	CMC ($g \cdot dl^{-1}$) (pH 6.8) x 10^3	CMC ($g \cdot dl^{-1}$) (pH 4.0) x 10^3
20	10.000	8.00	8.00	8.00
25	8.00	-	-	-
30	7.00	-	-	-
37	7.00	7.00	7.00	7.00
40	6.00	-	-	-

buffered aqueous solutions of the surfactants (Tables 1,3). As the pH of the substrate was increased, the CMC remained constant at 20°C and also at 37°C.

The surface tensions of the two surfactants, Simulsol OL 50 and Simulsol 98, in the presence of 0.05 M borate, phosphate and phthalate buffers, were decreased when compared to the CMC obtained in water (Tables 1,3 and Figures 2,4). As seen in Tables 1 and 3, there is a ten fold difference between the CMC of the two surfactants.

The solubilities of Simulsol OL-50 and Simulsol 98 at 25°C in distilled water, corn oil, and 0.05 M buffer solutions are shown in Tables 2 and 4, respectively.

The densities of Simulsol OL-50 and Simulsol 98 are 1057.0 Kgm^{-3} and 1040.0 Kgm^{-3}, respectively.

TABLE 2

THE SOLUBILITY TENDENCIES OF DIFFERENT CONCENTRATIONS (% W/W) OF SIMULSOL OL - 50 AT 25°C.

Substrate	Solubility Tendencies									
	5%	10%	15%	20%	25%	30%	35%	40%	45%	50%
Distilled water	S + CL	S + CL	S + PY	S + PY	S+V+Y	S+V+Y	S+V+Y	S+V+Y	S+V+Y	S+V+Y
pH 4.0 buffer	S + CL	S + CL	S + PY	S + PY	S+V+Y	S+V+Y	S+V+Y	S+V+Y	S+V+Y	S+V+Y
pH 6.8 buffer	S + CL	S + CL	S + PY	S + PY	S+V+Y	S+V+Y	S+V+Y	S+V+Y	S+V+Y	S+V+Y
pH 9.2 buffer	S + CL	S + CL	S + PY	S + PY	S+V+Y	S+V+Y	S+V+Y	S+V+Y	S+V+Y	S+V+Y
Corn Oil	D	D	D	D	D	D	D	D	D	D

S = Soluble

D = Dispersable

S + CL = Soluble + Clear white

S + PY = Soluble Pale yellow

S + V + Y = Soluble Viscos Yellow

TABLE 3

THE CRITICAL MICELLE CONCENTRATION OF SIMULSOL 98 IN AQUEOUS SOLUTIONS AND AT DIFFERENT pH'S OF VARIOUS TEMPERATURES

Temp. °C	CMC($g.dl^{-1}$) water X 10^3	CMC($g.dl^{-1}$) (pH 9.2) X 10^3	CMC($g.dl^{-1}$) (pH 6.8) X 10^3	CMC($g.dl^{-1}$) (pH 4.0) X 10^3
20	3.0	0.9	0.9	0.8
25	2.0	-	-	-
30	2.0	-	-	-
37	1.0	0.8	0.7	0.7
40	1.0	-	-	-

Ultra-Violet and Infra-Red spectra of the two surfactants are also determined.

U.V. spectra of Simulsol 98 and Simulsol OL-50 show a maximum peak at 232 and 234-236, respectively. Infra-Red spectra of Simulsol OL-50 is in accordance with Müller's(8) investigation.

DISCUSSION

Simulsol OL-50 (EO 40) and Simulsol 98 (EO 20) are nonionic surfactants which are readily soluble in water and in aqueous buffer solution. As the pH increases there is no change in the aqueous solubility tendencies (Tables 2 and 4).

CMC would be expected to increase as the temperature increases due to a thermal agitation decreasing adhesion between monomers. This is true for ionized surfactants at higher temperatures. At lower temperatures the CMC decreases with increasing temperatures probably due to desolvation of parts of the monomer (4,6,9). For

TABLE 4

THE SOLUBILITY TENDENCIES OF DIFFERENT CONCENTRATIONS (% W/W) OF SIMULSOL 98 AT 25°C

Subtrate	Solubility tendencies									
	5%	10%	15%	20%	25%	30%	35%	40%	45%	50%
Distilled water	S	S	S	S	G	G	G	G	G	G
pH 4.0 buffer	S	S	S	S	G	G	G	G	G	G
pH 6.8 buffer	S	S	S	S	G	G	G	G	G	G
pH 9.2 buffer	S	S	S	S	G	G	G	G	G	G
Corn Oil	Su	Su	Su	I	I	I	I	I	I	I

S = Soluble I = Insoluble

Su = Suspended G = Gel

nonionic surfactants, the CMC decreases with temperature up to the highest value measured, indicating that desolvation effect on polyoxyethylene chains of the monomer, may be so large that they over weigh effects of thermal agitation in breaking up the micelles (4). This is supported by the CMC versus temperature curve (Figure 5). The CMC of Simulsol OL-50 and 98 decreases with temperature range of 20-40°C. The CMC of Simulsol 98 is in accordance with Becker's work (2).

The effect of electrolytes on nonionic surfactants in generally to lower the CMC, probably because of electrostatic screening action by salts (1,4). The 0.05 M phthalate, phosphate and borate buffers lowered the CMC by an order of magnitude from that measured in water in both of the surfactants (Figures 2,4 and Tables 1,3).

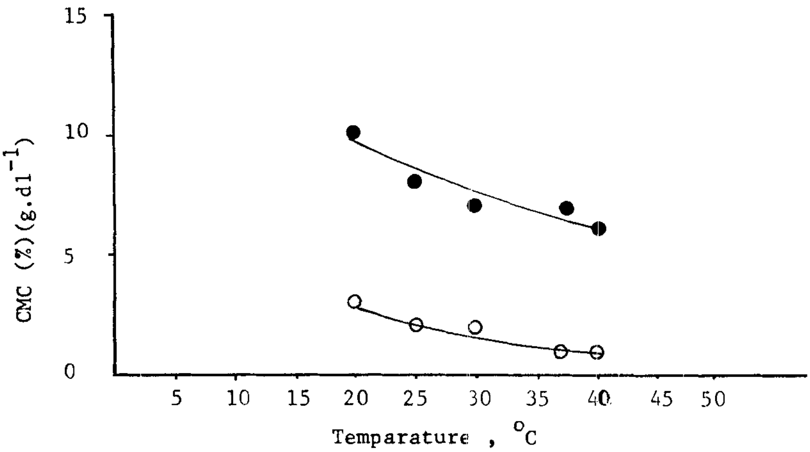

FIGURE 5

The effect of temperature on the aqueous CMC of Simulsol OL 50 and Simulsol 98

● Sim. OL - 50
○ Sim. 98

Measurement of the surface tension of increasing concentrations of buffered solutions, especially 0.05 M phthalate buffer, showed a slight depression at the inflection point associated with the CMC, (Figure 4), suggesting the presence of small quantities of impurities. This is due to the impurities adsorbed at the surface below the CMC, but solubilized by the micelles beyond the CMC(10).

The solubilities, CMC versus temperature curves and the effect of electrolytes on CMC, all support that the behaviour of our surfactants is typical of a nonionic surfactants.

ACKNOWLEDGEMENTS

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