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# The Relationship Between Surface Effects Due to Electrolytes and Emulsion Stability

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**Synopsis**—It is shown that the addition of electrolytes to emulsions can alter specific parameters which, in turn, can be related to emulsion stability. A mechanism for the action of specific electrolytes on emulsion systems containing certain nonionic polyoxyethylene ethers as emulsifiers is postulated. The surface chemistry effects which result from the included salts are discussed.

## INTRODUCTION

The cosmetic chemist may often be required to formulate an emulsion containing an electrolyte. A wide variety of suitable emulsifiers is available for this purpose. However, the presence of electrolytes, even in small quantities, will often cause changes in the surface chemistry of commonly employed emulsifiers and seriously affect the stability of the product.

The difficulties created by the inclusion of electrolytes may be elusive. A nonionic emulsifier, e.g., an ethylene oxide condensate, is often selected to overcome the formulation problems which may arise due to the presence of electrolyte. However, this approach, too, must be carefully considered. Although the literature concerning the effect of electrolytes on emulsifiers is extensive, the investigators generally

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were concerned more with electrolyte-emulsifier interactions rather than their effect on the emulsion system (1–3).

In this paper it will be shown that, in formulations containing certain nonionic ethoxylates, emulsion stability may be enhanced or diminished by the addition of specific quantities of various electrolytes. From a study of variations of surface-related measurements of several polyoxyethylene ethers by added electrolytes, a mechanism of electrolyte emulsion interactions may be postulated.

## EXPERIMENTAL

The surface-active materials used in the formulations were a series of ethoxylated fatty alcohols. The Siponics®,* in which the series number is multiplied by 2 to obtain the degree of ethoxylation, were used. The exceptions to this rule are Siponic EO and Siponol TX®*; the former contains one molecule of ethylene oxide and the latter none. The ethylene oxide content of the emulsifiers used in the experimental formulations ranged from 10 to 30 molecules per fatty alcohol molecule. The ethoxylates were the sole emulsifiers used in all formulations. All added electrolytes were reagent grade.

### *Preparation of Emulsions*

The formulations were made by combining two emulsion phases. The electrolytes were placed in the aqueous phase, while mineral oil (65/75 Saybolt) and ethoxylate were considered to be the oil phase. This procedure was used because, in a preliminary series, conductivity and dispersibility measurements indicated that the particular ethoxylates chosen formed O/W emulsions. It was also ascertained that emulsion stability was somewhat enhanced when the ethoxylate was included in the oil phase. All the electrolytes were water-soluble. The two emulsion phases were placed separately in two 1500 ml Pyrex beakers and heated in a hot water bath to 80 ± 1 °C. The water phase was then added to the oil phase slowly in a thin stream. A four-blade propeller, which was inserted to a depth of 3.8 cm below the emulsion surface, was used for agitation. The propeller speed was kept constant at 100 rpm. The product was formulated in an air-conditioned laboratory at 25 ± 1 °C and 40 ± 5% relative humidity. Continuous agitation was maintained during air cooling. The experimental emulsions were designed so that at completion each weighed 1000 g. Aliquots of

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* Siponic and Siponol are registered trade names of Alcolac Chemical Corp., Baltimore, Md. 21226

50 g of each completed formulation were placed in several glass vials and immediately sealed.

### *Measurements*

Subjective observations and objective parameter measurements were conducted on material obtained from these vials. Particle size determinations of approximately 500 emulsion droplets, the oil phase of which was stained by Sudan Red, were carried out by means of a microscope equipped with a stage micrometer. The measurements were conducted, wherever sufficient emulsion stability permitted, 30 minutes after the emulsion had reached ambient (25 ± 1 °C) temperature. pH measurements were made with a Beckman Zeromatic pH meter immediately after complete cooling of the formulation and also 24 hours later.

Critical micelle concentration (C.M.C.) data of individual ethoxylates and of ethoxylate-electrolyte combinations were obtained on aqueous solutions of individual ethoxylates and ethoxylate-electrolyte combinations. The individual ethoxylate was added in exponentially increasing concentration to deionized water. In the case of ethoxylate-electrolyte combinations, the exponential dilutions were carried out in aqueous solutions with deionized water containing the proper concentration of electrolyte. This procedure was repeated with several electrolyte concentrations to assess the effect on the C.M.C. Exactly 0.1 ml of a 0.5% aqueous dye solution, Benzopurpurin 4B (a biological stain from Matheson, Coleman and Bell), was then added to 100 ml aliquots of each of the solutions. The transmittance of these solutions was measured on a Bausch & Lomb Spectronic 20 at 540 m$\mu$. A curve for each ethoxylate (where sufficient solution clarity permitted) and ethoxylate-electrolyte combination was plotted (Figs. 1–4). A sharp change in the slope of the curve over a narrow ethoxylate concentration was observed. This variance, in accordance with the experimental results of Becher and Schmolka and Raymond, can be assumed to occur at the C.M.C. (4, 5).

Surface tension studies were made with the DuNouy tensiometer. Aqueous solutions, consisting of exponential dilutions of individual ethoxylates and ethoxylate-electrolyte combinations prepared in a manner similar to that used for the C.M.C. studies, were utilized in determining surface tensions (Figs. 5–13). Moreover, the results from the tensiometer were compared to the C.M.C. data obtained with the dye to determine agreement of the methods in the presence of electrolyte.

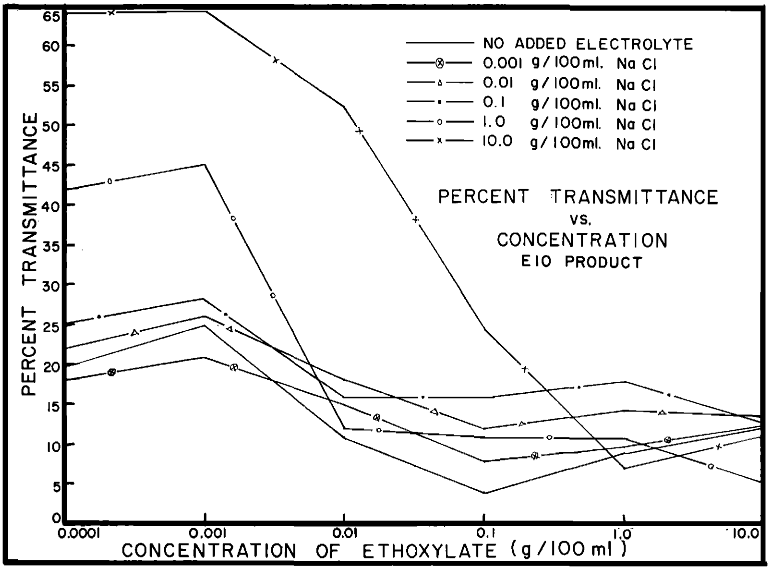

*Figure 1.* Variation of transmittance as a function of concentration of E10 ethoxylate in the presence of sodium chloride

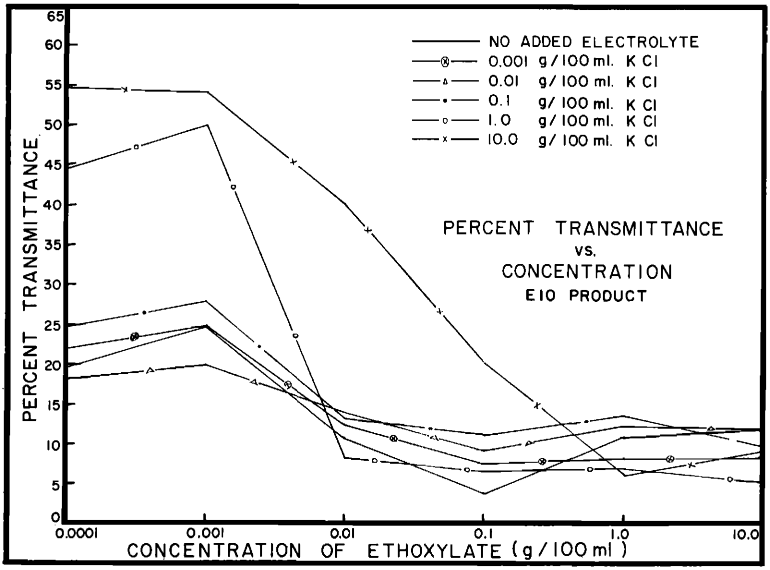

*Figure 2.* Variation of transmittance as a function of concentration of E10 ethoxylate in the presence of potassium chloride

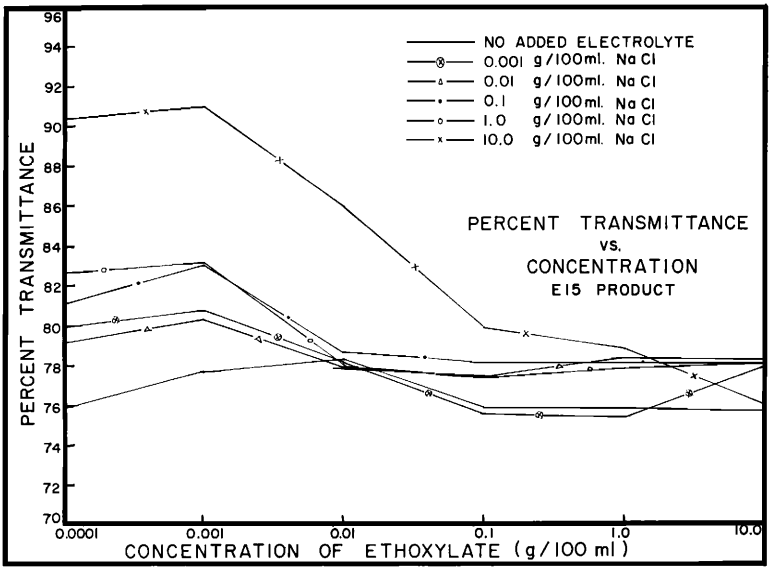

*Figure 3.* Variation of transmittance as a function of concentration of E15 ethoxylate in the presence of sodium chloride

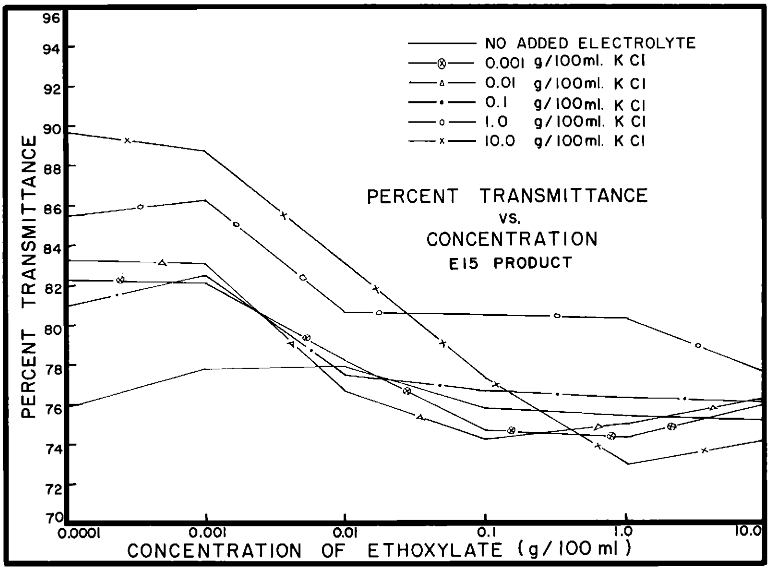

*Figure 4.* Variation of transmittance as a function of concentration of E15 ethoxylate in the presence of potassium chloride

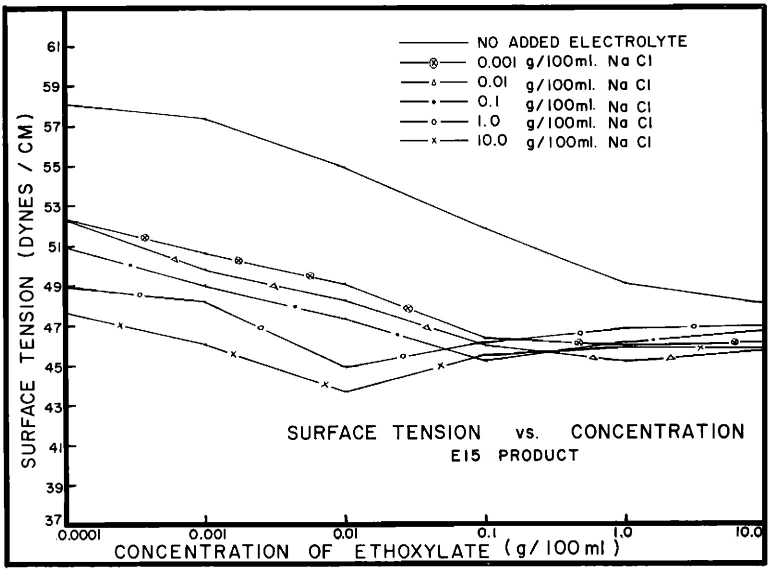

*Figure 5.* Variation of surface tension as a function of concentration of E15 ethoxylate in the presence of sodium chloride

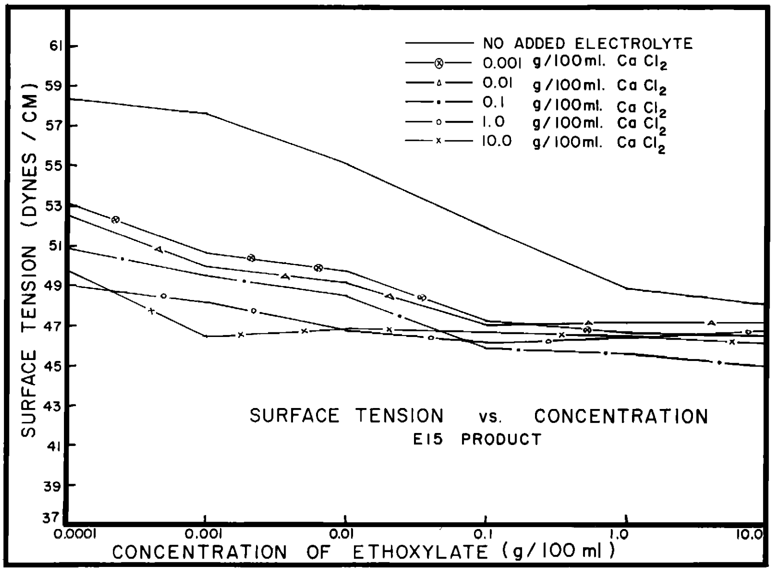

*Figure 6.* Variation of surface tension as a function of concentration of E15 ethoxylate in the presence of calcium chloride

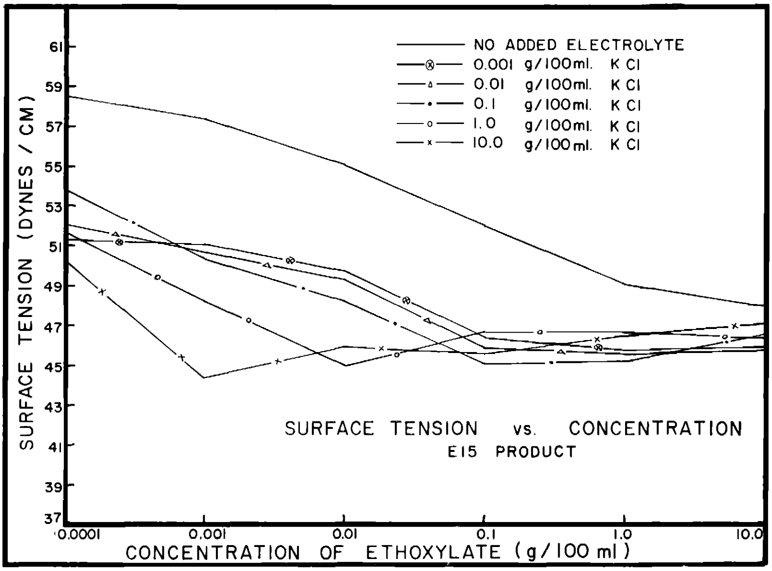

*Figure 7.* Variation of surface tension as a function of concentration of E15 ethoxylate in the presence of potassium chloride

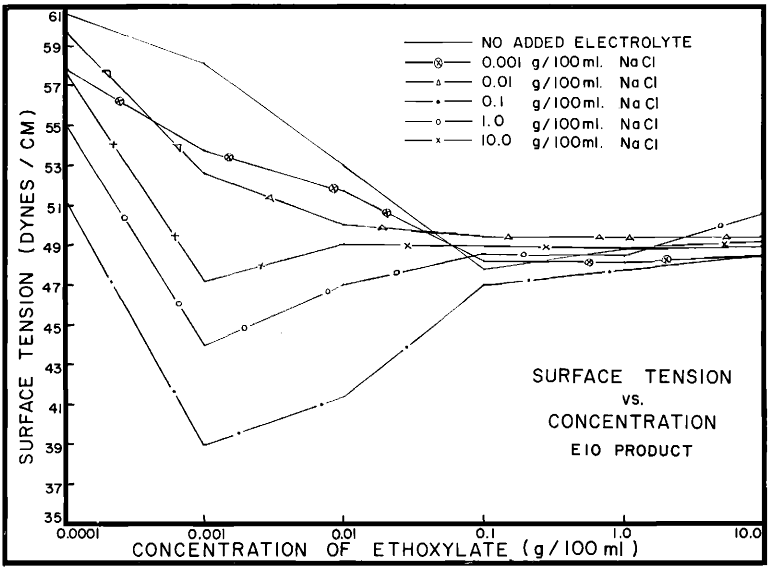

*Figure 8.* Variation of surface tension as a function of concentration of E10 ethoxylate in the presence of sodium chloride

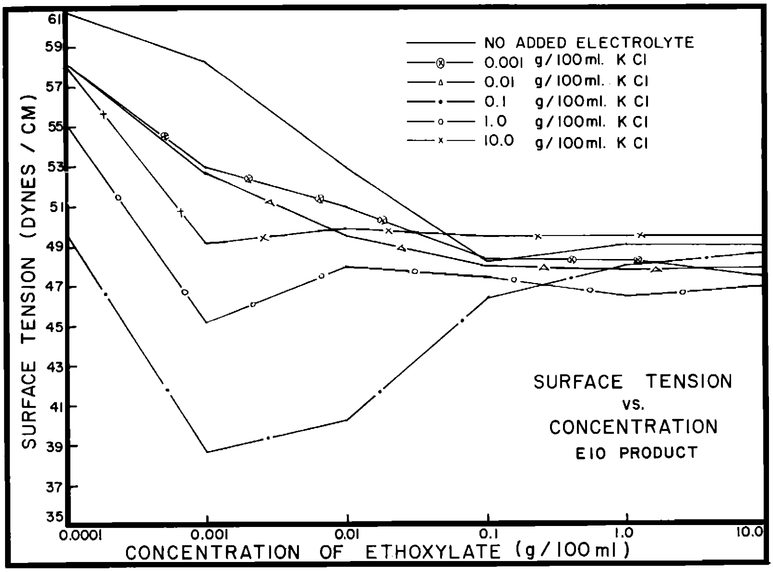

*Figure 9.* Variation of surface tension as a function of concentration of E10 ethoxylate in the presence of potassium chloride

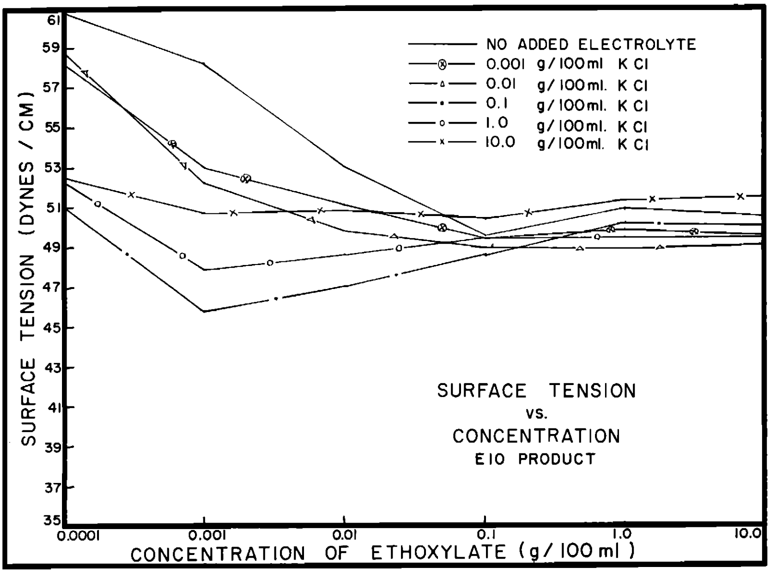

*Figure 10.* Variation of surface tension as a function of concentration of E10 ethoxylate in the presence of calcium chloride

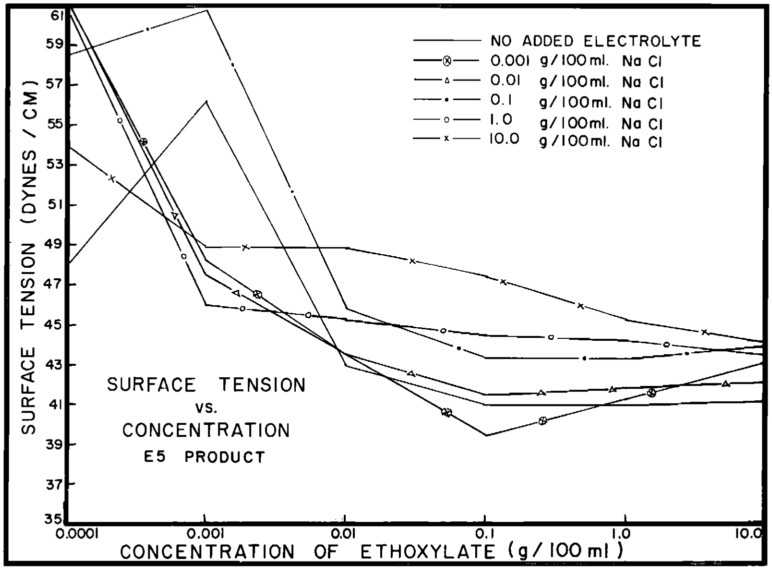

*Figure 11.* Variation of surface tension as a function of concentration of E5 ethoxylate in the presence of sodium chloride

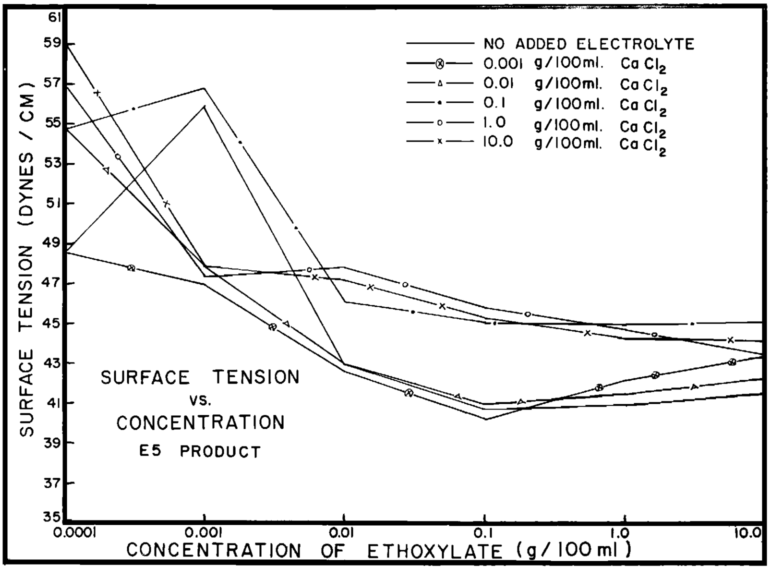

*Figure 12.* Variation of surface tension as a function of concentration of E5 ethoxylate in the presence of calcium chloride

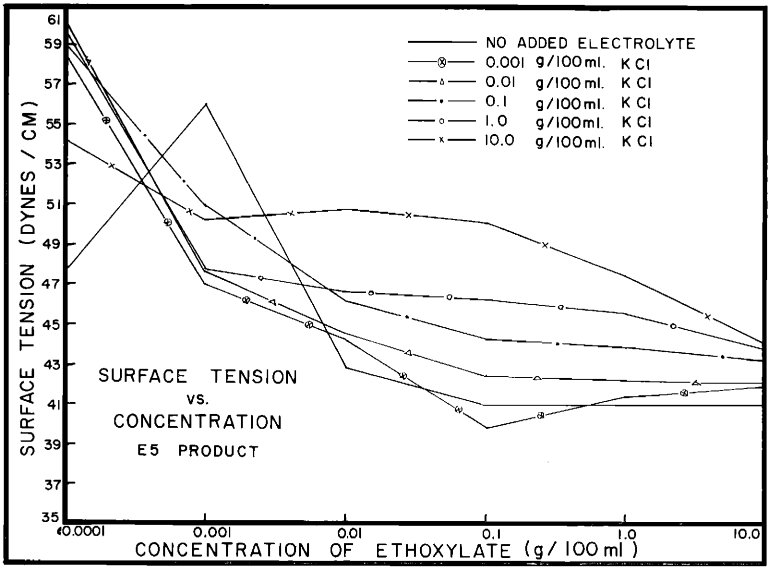

*Figure 13.* Variation of surface tension as a function of concentration of E5 ethoxylate in the presence of potassium chloride

There was, in most cases, fair agreement between the two methods.

Emulsion type was determined from electrical conductivity, aqueous dispersibility, and microscopic examination of the completed emulsions. Sudan Red, as previously mentioned, was added to the oil phase of the formulations. Microscopic observations of the experimental formulations were used to determine which phase of the emulsion was dye-stained. Emulsion type was then classified on the basis of agreement among the several methods. The measurements of emulsion type were taken 30 minutes after completion of the formulation.

To eliminate the possibility of affecting the experimental results through the ethoxylate mineral oil ratio, several variations were studied. The presented formulations have large ethoxylate/mineral oil ratios. Therefore, several emulsions were formulated in which the percentage of mineral oil was kept constant and the amount of ethoxylate was reduced from 10 to 7%. A second approach to reducing the ratios consisted of increasing the mineral oil while the percentage of ethoxylate was held constant at 10%. Emulsions in this series were formulated with 10% mineral oil. The results obtained, where measurements were possible, indicated that ratio variations did not significantly alter the experimental results. Therefore, it was concluded that the electrolyte-emulsifier interactions were similar and affected the emulsion parameters in the same manner over several ratio variations.

Data on particle size, pH, emulsion type, and viscosity were obtained from two series of experimental emulsions as follows:

A. Each member of this series contained the single ethoxylate. Electrolyte was not included in any emulsions of this series. Formulations consisted of only three components:

| | |
|---|---|
| 1. E15, E10, or E5 ethoxylate | 10% by wt. |
| 2. Mineral oil (65/75 Saybolt) | 5% by wt. |
| 3. Deionized water | 85% by wt. |

B. Members of this series contained one single ethoxylate. However, electrolyte was included in varying concentration in all formulations:

| | |
|---|---|
| 1. E15, E10, or E5 ethoxylate | 10% by wt. |
| 2. Mineral oil (65/75 Saybolt) | 5% by wt. |
| 3. Calcium, potassium, or sodium chloride | 0.001%, 0.01%, 0.1%, 1.0%, or 10.0% by wt. |
| 4. Deionized water | q.s 100% |

## Discussion of Experimental Results

Microscopic observations of the internal phase indicated a variation in mean particle diameter which was influenced by the choice of the ethoxylate and the nature and quantity of electrolyte (Tables I–III). In emulsions which contained the ethoxylate in the absence of added electrolyte, the E5 product formed particles of smaller mean diameter than did the E15 or E10 ethoxylates. The significance of this observation was pointed out in an earlier publication (6). Experimental emulsions which contained the E5, E10, and E15 ethoxylates together with increasing concentrations of potassium, sodium, and calcium chlorides exhibited distinct variations in particle size. With increasing concentrations of sodium, potassium, or calcium chlorides the mean diameter of the particle decreased. A direct relationship was observed between diminishing particle size and increasing electrolyte concentration up to 10%. Further studies were undertaken at a later date in which the electrolyte content was increased to 20%. In the case of the E10 and E15 products, there was further reduction in the mean emulsion particle diameters. In the case of the E5 formulations, 20% of sodium, potassium, or calcium chloride increased the particle size.

Table I

Parameters of Emulsions Prepared with E5 Ethoxylate

| Formulation (Emulsifier and Electrolyte Content) | pH (Beckman Zeromatic) 30 min after Completion | Viscosity (Brookfield LVF No. 4 Spindle 60 rpm at 25°C; in cps) | Mean Particle Diameter, 30 min after Completion (μ) | Emulsion Type |
|---|---|---|---|---|
| 1. E5, no electrolyte | 5.8 | 50 | 4.3 | O/W |
| 2. E5, 0.001 g/100 ml sodium chloride | 5.8 | 50 | 4.3 | O/W |
| 3. E5, 0.01 g/100 ml sodium chloride | 5.8 | 55 | 4.2 | O/W |
| 4. E5, 0.1 g/100 ml sodium chloride | 5.7 | 60 | 3.8 | O/W |
| 5. E5, 1.0 g/100 ml sodium chloride | 5.7 | 170 | 2.9 | O/W |
| 6. E5, 10 g/100 ml sodium chloride | 5.6 | 300 | 2.0 | O/W |
| 7. E5, 0.001 g/100 ml potassium chloride | 5.9 | 50 | 4.0 | O/W |
| 8. E5, 0.01 g/100 ml potassium chloride | 5.6 | 45 | 3.5 | O/W |
| 9. E5, 0.1 g/100 ml potassium chloride | 5.5 | 60 | 3.3 | O/W |
| 10. E5, 1.0 g/100 ml potassium chloride | 5.4 | 55 | 2.7 | O/W |
| 11. E5, 10 g/100 ml potassium chloride | 5.3 | 100 | 2.0 | O/W |
| 12. E5, 0.001 g/100 ml calcium chloride | 4.4 | 50 | 4.5 | O/W |
| 13. E5, 0.01 g/100 ml calcium chloride | 4.4 | 55 | 4.4 | O/W |
| 14. E5, 0.1 g/100 ml calcium chloride | 4.3 | 70 | 4.1 | O/W |
| 15. E5, 1.0 g/100 ml calcium chloride | 3.8 | 100 | 3.9 | O/W |
| 16. E5, 10 g/100 ml calcium chloride | 3.5 | 150 | 3.0 | O/W |

Table II

Parameters of Emulsions Prepared with E10 Ethoxylate

| Formulation (Emulsifier and Electrolyte Content) | pH (Beckman Zeromatic) 30 min after Completion | Viscosity (Brookfield LVF No. 4 Spindle 60 rpm at 25°C; in cps) | Mean Particle Diameter, 30 min after Completion ($\mu$) | Emulsion Type |
|---|---|---|---|---|
| 1. E10, no electrolyte | 6.0 | 40 | 10.0 | O/W |
| 2. E10, 0.001 g/100 ml sodium chloride | 6.1 | 40 | 10.0 | O/W |
| 3. E10, 0.01 g/100 ml sodium chloride | 6.0 | 50 | 8.8 | O/W |
| 4. E10, 0.1 g/100 ml sodium chloride | 5.9 | 43 | 8.7 | O/W |
| 5. E10, 1.0 g/100 ml sodium chloride | 6.1 | 60 | 8.7 | O/W |
| 6. E10, 10 g/100 ml sodium chloride | 5.6 | 45 | 5.0 | O/W |
| 7. E10, 0.001 g/100 ml potassium chloride | 5.8 | 45 | 10.0 | O/W |
| 8. E10, 0.01 g/100 ml potassium chloride | 5.7 | 30 | 8.6 | O/W |
| 9. E10, 0.1 g/100 ml potassium chloride | 5.7 | 33 | 8.5 | O/W |
| 10. E10, 1.0 g/100 ml potassium chloride | 5.6 | 40 | 6.5 | O/W |
| 11. E10, 10 g/100 ml potassium chloride | 5.5 | 50 | 3.8 | O/W |
| 12. E10, 0.001 g/100 ml calcium chloride | 4.6 | 30 | 10.0 | O/W |
| 13. E10, 0.01 g/100 ml calcium chloride | 4.7 | 38 | 9.5 | O/W |
| 14. E10, 0.1 g/100 ml calcium chloride | 4.7 | 31 | 9.4 | O/W |
| 15. E10, 1.0 g/100 ml calcium chloride | 4.5 | 50 | 8.5 | O/W |
| 16. E10, 10 g/100 ml calcium chloride | 4.0 | 42 | 6.0 | O/W |

Table III

Parameters of Emulsions Prepared with E15 Ethoxylate

| Formulation (Emulsifier and Electrolyte Content) | pH (Beckman Zeromatic) 30 min after Completion | Viscosity (Brookfield LVF No. 4 Spindle 60 rpm at 25°C; in cps) | Mean Particle Diameter, 30 min after Completion ($\mu$) | Emulsion Type |
|---|---|---|---|---|
| 1. E15, no electrolyte | 6.0 | 33 | 10.0 | O/W |
| 2. E15, 0.001 g/100 ml sodium chloride | 6.0 | 38 | 9.7 | O/W |
| 3. E15, 0.01 g/100 ml sodium chloride | 5.9 | 37 | 8.9 | O/W |
| 4. E15, 0.1 g/100 ml sodium chloride | 6.0 | 41 | 8.5 | O/W |
| 5. E15, 1.0 g/100 ml sodium chloride | 5.8 | 40 | 7.9 | O/W |
| 6. E15, 10 g/100 ml sodium chloride | 5.5 | 43 | 5.8 | O/W |
| 7. E15, 0.001 g/100 ml potassium chloride | 6.0 | 29 | 10.0 | O/W |
| 8. E15, 0.01 g/100 ml potassium chloride | 6.1 | 30 | 9.7 | O/W |
| 9. E15, 0.1 g/100 ml potassium chloride | 6.2 | 34 | 9.4 | O/W |
| 10. E15, 1.0 g/100 ml potassium chloride | 6.2 | 38 | 8.5 | O/W |
| 11. E15, 10 g/100 ml potassium chloride | 5.7 | 50 | 5.0 | O/W |
| 12. E15, 0.001 g/100 ml calcium chloride | 6.0 | 45 | 9.8 | O/W |
| 13. E15, 0.01 g/100 ml calcium chloride | 6.0 | 49 | 9.4 | O/W |
| 14. E15, 0.1 g/100 ml calcium chloride | 6.1 | 43 | 9.1 | O/W |
| 15. E15, 1.0 g/100 ml calcium chloride | 5.0 | 41 | 7.9 | O/W |
| 16. E15, 10 g/100 ml calcium chloride | 4.5 | 40 | 7.0 | O/W |

By applying Stokes' equation to the experimental formulations, those in a given series which exhibited a reduction in the mean particle diameter would be expected to have relatively reduced creaming or sedimentation rates, assuming all other variables remained constant (7). Further microscopic study of the emulsions revealed that all possessed a highly agglomerated internal phase. However, agglomeration at emulsifier concentrations in excess of the C.M.C. is not unusual (8). Agglomeration does not necessarily hasten coalescence, and Van der Waals' attractive forces (in the absence of marked electrostatic repulsion, a situation which exists in these experimental emulsions) cause rapid particle agglomeration. However, as the agglomerated emulsion particles coalesce, those emulsions which have a large initial particle size may exhibit rapid visual evidence of coalescence, observable as an increasing transparent surface layer.

Calcium chloride produced somewhat different, although parallel, emulsion parameter variations from those observed with sodium or potassium chloride. In this case the particle size in the E5, E10, and E15 experimental formulations diminished with increasing concentration, but the reduction was less pronounced than that induced by sodium or potassium chloride.

Emulsion type, where sufficient stability permitted this determination, was O/W in all cases. Measurements taken at the specified interval of 30 minutes by any of the methods were in complete agreement.

The pH measurements conducted 24 hours after completion of the experimental formulations did not show any marked variations from those taken immediately after cooling.

Surface tension data compiled with the aid of the DuNouy tensiometer in the absence of added electrolyte revealed that the E5 ethoxylate produced a somewhat lower value (at the C.M.C.) than the E10 or E15 ethoxylates. It was further ascertained that emulsions with E10 possessed a somewhat lower surface tension (at the C.M.C.) than those with the E15 ethoxylate. A decrease in the surface tension at the C.M.C. was evident in specific instances with increasing concentrations of electrolyte. The phenomenon was observed in the formulations containing the E15, E10, and E5 ethoxylates. The decrease continued until a limiting concentration was added. Further additions of electrolytes (in excess of the optimal or limiting concentration) raised the surface tension. The experimental data obtained with the DuNouy tensiometer disclose a direct relationship between the ethoxylate series number and the optimum quantity of added electrolyte which yields the lowest surface tension at the C.M.C.; that is, the E5 product exhibits its lowest C.M.C. surface tension at 0.001 g/100 ml of electrolyte, the E10 at 0.1 g/100 ml, and the E15 formulation at 10.0 g/100 ml. Formulations containing sodium or potassium chloride in combination with the E10, E15, and E5 ethoxylates presented somewhat lower surface tensions at the C.M.C. at optimal (0.001 g/100 ml for the E5, 0.1 g/100 ml for the E10, and 10.0 g/100 ml for the E15) electrolyte concentrations than those given by limiting quantities of calcium chloride. Relative to their C.M.C. surface tensions in the absence of included electrolyte, the E15 and E10 formulations exhibited greater reductions of surface tension than the E5 compositions after addition of optimum quantities of electrolyte (Figs. 5–13).

In the absence of any electrolyte, C.M.C.s, determined by both dye and tensiometer methods, decrease with decreasing ethoxylate series number. In most cases, the inclusion of electrolyte was accompanied by decreases in the C.M.C. The decreases were directly related to the quantity of electrolyte. Exceptions were noted at 10% electrolyte when the dye method was used; it is postulated that inclusion of 10% electrolyte may have interfered with the validity of the results obtained by this procedure (Figs. 1–4).

It is also suggested, through correlation of decreases in C.M.C. surface tension, that specific quantities of electrolyte included in the presented experimental emulsions containing the E5, E15, and E10 ethoxylates cause increased interfacial coverage by the emulsifier through interactions favoring a decrease in the area occupied by the individual ethoxylate molecule.

The ethoxylates used in the experimental formulations function by tightly binding water to the surface of the dispersed or oil phase (9). Coalescence of the dispersed oil droplets would occur if this water of hydration is displaced and if the emulsifier is desorbed into the internal phase. This mechanism is postulated on the premise that steric hindrance would prevent the desorption of emulsifier into the continuous or water phase. Ethoxylate desorption and ultimate particle coalescence are retarded by the presence of an energy barrier which depends upon the number and type of hydrated groups on each molecule of the emulsifying agent and on the fraction of the interface covered (9). The greater the number of hydrated groups the greater is the energy barrier to displacement of water of hydration and ethoxylate desorption.

For optimum emulsion stability, it is essential that the ethylene oxide groups on the cetyl/stearyl alcohol not only hydrate with water molecules but occupy the greatest possible fraction of the emulsion interface. Therefore, the emulsifier should not only undergo maximum interfacial adsorption (thereby occupying the greatest fraction of the emulsion interface) but form a coherent desorption-resistant film. Since the ethoxylate will reduce surface tension, adsorption will occur, as postulated in Gibbs' adsorption equation (7). Adsorption does not increase infinitely in direct proportion to the quantity of ethylene oxide on the ethoxylate molecule. Adsorption and, consequently, interfacial coverage increase to a finite maximum with increasing ethylene oxide content. Increases beyond a limiting optimal quantity will, however, result in decreasing adsorption. A conflict arises between resistance to desorption, which depends only on number and type of hydrated groups, and interfacial adsorption, which depends on an optimal hydration energy.

The addition of electrolyte to the experimental formulations will inhibit hydration of ethylene oxide groups. The presence of ions, released by the addition of electrolyte, will cause water molecules to be drawn toward themselves and prevent them from participating in hydrogen bonding with other neighboring water molecules (10). Because of its interaction with the water molecules, the electrolyte reduces the energy of hydration and solubility of the ethoxylates. Even though hydration energy and solubility are decreased by added electrolyte, the experimental emulsions with the E15, E10, and E5 ethoxylates and with specific quantities of sodium, potassium, or calcium chlorides may show enhanced emulsion stability because of the nature of C.M.C. surface tension and particle size variations created by the included electrolyte. As mentioned earlier, surface tension data indicated reduced C.M.C.s and, consequently, increased ethoxylate adsorption in those formulations containing the E15, E10, and E5 ethoxylates in the presence of optimal quantities of electrolyte. Also, particle size variations (due to inclusion of specific electrolyte concentrations) suggest decreased creaming velocities on the basis of Stokes' equation.

Further clarification of the experimental results can be obtained by mathematical justification of the enhanced stability observed in experimental formulations containing electrolyte in conjunction with the E15, E10, and E5 ethoxylates (Tables I–III).

Gibbs' adsorption isotherm can be expressed thusly:

$$\Gamma = -\frac{c}{KT} \cdot \frac{d\gamma}{dc},$$

where:

$c$ = concentration of the ethoxylates
$K$ = constant
$T$ = absolute temperature
$\gamma$ = surface tension
$\Gamma$ = surface concentration of the adsorbed monolayer.

Stokes' law, relating creaming and sedimentation velocity to specific emulsion variables, may be expressed mathematically as follows:

$$V = \frac{4/3\pi r^3 g(d_1 - d_2)}{6\pi n r},$$

where:

$V$ = rate of creaming or sedimentation
$r$ = droplet radius
$g$ = acceleration of gravity
$d_1$ = density of the droplet
$d_2$ = density of the liquid
$n$ = viscosity of the dispersion medium.

Application of Gibbs' adsorption isotherm to the experimental formulations shows that the adsorption becomes more positive as surface tension decreases. As adsorption increases, the fraction of the interface covered by the ethoxylate may increase. Theoretically, a reduced rate of coalescence and enhanced stability should result. According to Stokes' equation, an inverse relationship exists between the particle radius and creaming velocity. Experimental emulsions in which the radii of the particles of the internal or dispersed phase are smaller than those of other members of the series should exhibit higher stability (assuming that other variables in the equation remain constant). In the specific instances cited above, the influence of added electrolyte on the C.M.C., surface tension, mean particle diameter of the dispersed phase, and to a minor extent (in the case of the experiments presented here) on emulsion viscosity is such as to cause possibly enhanced emulsion stability.

## CONCLUSION

The direction of parameter variation due to added electrolyte is influenced primarily by the ethylene oxide content of the fatty alcohol.

Ethoxylate adsorption and interfacial coverage reach a maximum with a specific, as determined by ethylene oxide content, hydration energy; above or below the limiting optimal hydration energy reduced adsorption results. The E15, E10, and E5 ethoxylates have hydration energies determined to a large extent by their ethylene oxide content. The presence of added sodium, potassium, or calcium chloride reduces this hydration energy. However, in the case of the E15, E10, and E5 ethoxylates, their ethylene oxide content may be—by correlation of the variations in surface tension observed at the C.M.C. in the presence of electrolyte—greater than that required for optimal adsorption. It is also suggested that the reduction of the greater than optimal hydration energy through the addition of electrolyte can be related, in specific instances, to particle size reductions. Added electrolyte reduced the hydration energy of the E15, E10, and E5 ethoxylates by disrupting ethoxylate-water molecule interactions. However, in the case of formulations containing the E15, E10, and E5 ethoxylates, the hydration energy is effectively reduced by electrolytes to the point of optimal stability. It is suggested that, since the ethylene oxide content of the E5 product is less than that of E10 or E15, smaller quantities of electrolyte are required to induce parameter variations associated with optimum stability. However, at electrolyte content greater than the 10% experimental limits the variations can be associated with still better emulsion stability in the case of the E15 and E10 products instead of deterioration as might occur with the E5 ethoxylate.

Examination of the experimental data indicates that the surface parameter variations caused by sodium or potassium chloride were similar but of different magnitude than those brought about by the addition of calcium chloride. The pH's of formulations with E15, E10, and E5 ethoxylates and calcium chloride are lower than those of other emulsions. The ions released by the hydrolysis of calcium chloride result in acidic emulsion conditions. It has been claimed that aqueous solutions of inorganic acids have lower surface tensions than water (11, 12). This leads to the conclusion that the proton is adsorbed at the surface, a result which conflicts with that of other investigations (13). However, the proton adsorption theories do not satisfy the experimental results of this paper. Instead, it is postulated that the protons released through hydrolysis of calcium chloride are not strongly adsorbed. If they were adsorbed, competition for space at the emulsion interface might occur. In the presence of excess protons, the ethoxylate may not be adsorbed in those instances where interfacial coverage was enhanced by added electrolyte to as great an extent as is observed with electrolytes which do not release excess hydrogen ions. Even though emulsion and surface parameter variations indicate increased emulsion stability with the E15, E10, and E5 ethoxylates in the presence of added electrolyte, the nature of the variations are such that formulations which contain sodium or potassium chloride may have greater long range emulsion stability than those containing calcium chloride. In this instance, the hydration of the polyvalent calcium ion induced parameter variations which are associated with diminished stability relative to those created by potassium or sodium chloride.

## SUMMARY

The measurable effect of added electrolyte on emulsions containing ethylene oxide-fatty alcohol derivatives as primary emulsifiers depends on several factors and their interrelation.

1. The interaction of the electrolyte with the water molecules is an important factor. Added electrolyte disrupts ethoxylate-water molecule interactions. The presence of ions causes the water molecules to be drawn toward themselves. Hydrogen bonding among neighboring water molecules and hydration of the ethylene oxide groups of the ethoxylate molecules are inhibited. Consequently, the effective hydration energy and solubility of the ethoxylate are diminished.

2. Ethoxylate hydration energy will help determine the extent of adsorption, particle size, C.M.C., and surface tension at the C.M.C. The values of these factors, as determined by inherent or electrolyte-induced ethoxylate hydration energy, play a decisive role in the emulsion's resistance to coalescence. By applying the numerical values for the above factors to Gibbs' adsorption isotherm and Stokes' creaming and sedimentation equation, the relative stability of the experimental formulas to coalescence can be predicted.

3. The quantity of electrolyte introduced into the experimental emulsions containing the E15, E10, and E5 ethoxylates determines emulsion stability. The presence of added electrolyte will reduce the hydration energy of the ethoxylate in a direct quantitative relationship. In those instances in which hydration energy is too great to be consistent with maximum interfacial adsorption, interfacial coverage (and as a consequence emulsion stability) increases with increasing amounts of electrolyte.

4. The nature of the electrolyte is also an important factor in projected emulsion stability. The inclusion of sodium or potassium chloride

in some cases induced greater positive emulsion parameter variations (indicative of possible increased long range stability) than those observed upon addition of calcium chloride. The ions released by hydrolysis of calcium chloride give rise to excess protons. It is postulated that protons are not strongly adsorbed at the emulsion interface and do not compete with the ethoxylate for interfacial sites. However, in formulations containing the E15, E10, and E5 ethoxylates calcium chloride does not produce emulsion parameter variations which indicate a degree of adsorption as great as that induced by optimal quantities of sodium or potassium chloride.

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