

# Effect of Inorganic Additives on Solutions of Nonionic Surfactants III: CMC's and Surface Properties

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**Abstract** □ Continuing work on the interaction of inorganic additives with nonionic surfactants in aqueous solution dealt with their effect on the CMC and surface tension. The surfactants were octoxynol and polyoxyethylated oleyl alcohol, containing an average of 9.5 and 10 ethylene oxide units, respectively. Their CMC values were lowered by most electrolytes studied, representing salting out of the surfactants. The steepest reductions in the CMC were produced by the nitrates of sodium and potassium, which had been found to lower the cloud points of nonionic surfactants, salting them out because of the inability of their cations to form complexes with the ether oxygen linkages of the polyoxyethylene moieties. However, even electrolytes with cations such as hydrogen, lithium, calcium, nickel, lead, and aluminum capable of forming complexes with the ether oxygens, thereby increasing the cloud points of the surfactants, lowered their CMC values. In the presence of increasing concentrations of the latter electrolytes, the CMC values frequently went through minima and approached the CMC of the surfactant in the absence of additives. Increases in the CMC over the entire range of additive concentrations investigated were produced by cadmium nitrate for octoxynol, urea for polyoxyethylated oleyl alcohol, and magnesium nitrate for both. Net increases in the plateau or micellar surface tension of polyoxyethylated oleyl alcohol, *i.e.*, in the constant surface tension of surfactant solutions above the CMC, were brought about by the nitrates of cadmium, aluminum, and magnesium at low concentrations only and by urea at all concentrations. This increase is interpreted as salting in. The area per surfactant molecule adsorbed at the air-water interface was reduced by all added electrolytes. Urea caused no such reduction.

**Keyphrases** □ Surfactants, nonionic—effect of inorganic additives on CMC and surface properties □ Inorganic additives—effect on CMC and surface properties, nonionic surfactant solutions □ CMC—nonionic surfactant solutions, effect of inorganic additives □ Surface properties—nonionic surfactant solutions, effect of inorganic additives

Recent studies of the effect of electrolytes on the cloud points of nonionic polyoxyethylated surfactants (1, 2) showed that increases, representing salting in of the surfactants, are far more common than reductions in the cloud point, representing salting out. Two categories of additives caused sizable increases in cloud points: (a) urea and salts with anions known to break the structure of water, such as iodides, thiocyanates, and perchlorates (2, 3); and (b) salts with cations capable of forming complexes with model ethers such as dioxane (1, 2). Polyoxyethylated surfactants, which contain many ether linkages, acted as polydentate ligands for these cations. The resulting complexation increased the solubility of the surfactant molecules in such salt solutions above that in water, raising their cloud points.

Electrolytes in the second category included strong acids and salts of lithium and of all polyvalent cations tested, namely, lead, cadmium, magnesium, nickel(II), aluminum, and calcium (1, 2). In fact, the only salts that lowered cloud points were those of noncomplexing cations (sodium, potassium, ammonium, cesium, and, probably, rubidium) with anions of lyotropic numbers (4) below 11.7. The anions included nitrate (lyotropic

number 11.6) but excluded perchlorate (lyotropic number 12.0) (1–3).

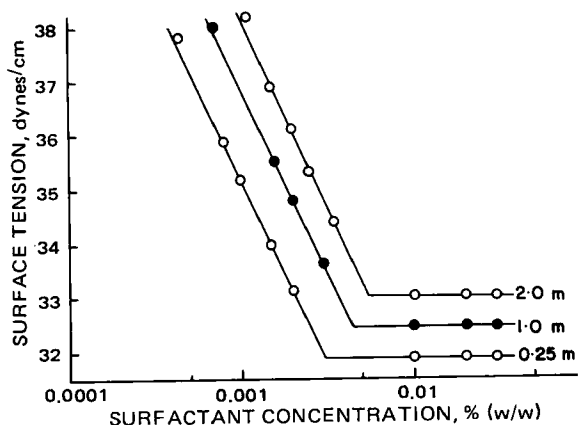
Most studies dealing with the effect of electrolytes on the critical micelle concentration (CMC) of polyoxyethylated nonionic surfactants reported a reduction in the CMC, corresponding to salting out (5). For instance, Hsiao *et al.* (6) found that all sodium salts examined depressed the CMC of nonoxynols (polyoxyethylated nonylphenols). The reduction in the CMC caused by the addition of 0.5 *N* sodium salts increased linearly with the decreasing lyotropic number of the anion; even sodium iodide lowered the CMC by nearly 30%. Becher (7, 8) found that 0.3 and 0.5 *N* sodium and calcium chloride, sodium citrate, and sodium sulfate lowered the CMC values of polyoxyethylated lauryl alcohol, tridecyl alcohol, and nonoxynol.

Schick and coworkers (3, 9) studied the effect of a variety of electrolytes, at the 0.86 *N* level, on the CMC of a nonoxynol. Only hydrochloric acid raised the CMC. The ability of the chlorides to lower the CMC increased in the order: lithium (41% reduction) < calcium < sodium < magnesium < potassium = strontium = barium < tetramethylammonium (59% reduction). For 0.86 *N* nitrates, the reduction in the CMC increased in the order: lithium < sodium < calcium = magnesium < potassium. For 0.86 *N* sodium salts with different anions, the reduction in the CMC increased in the order: thiocyanate (23% reduction) < iodide < nitrate = bromide < chloride < bromate < fluoride < citrate < sulfate (79% reduction).

While 0.5 *M* urea lowered the CMC of a nonoxynol by 18% (9), 3.0 and 6.0 *M* urea raised the CMC of that surfactant, as well as of polyoxyethylated lauryl and cetyl alcohols, by up to 200% at 25° (10, 11). The increases in the CMC were less pronounced at 45° than at 10°, because the structure of water is gradually disrupted by increasing temperatures even in the absence of urea. Guanidinium chloride and dioxane were even more effective than urea in raising the CMC of the nonoxynol (11), because they are even better structure breakers for water.

Measurements of sound velocity in solutions of polyoxyethylated octyl, nonyl, and decyl alcohols with added lithium chloride, bromide, or nitrate or potassium chloride revealed decreases in the CMC values as well as a narrowing in the concentration range over which micelles first appear (12).

Of the electrolytes of the second category (those with complex-forming cations), only hydrogen chloride has so far been found to increase the CMC of a polyoxyethylated surfactant. However, only three additional complexing cations have been studied, and only at single concentrations or over narrow concentration ranges. This prompted the investigation of the effect on the



**Figure 1**—Effect of cadmium nitrate on the surface tension of solutions of polyoxyethylated oleyl alcohol. Molalities (*m*) represent salt concentrations.

CMC of all those electrolytes of the second category that had demonstrated their ability to salt in polyoxyethylated surfactants by raising the cloud points. Relatively wide concentration ranges of added electrolytes were covered to spot trends in the variation of the CMC values.

### EXPERIMENTAL

Two nonionic polyoxyethylated surfactants were studied, octoxynol NF<sup>1</sup> (branched octylphenol with 9–10 ethylene oxide units) and oleyl alcohol with an average of 10 ethylene oxide units<sup>2</sup>. These two surfactants were designated as I and IV, respectively, in Ref. 2, where their formulas and properties were tabulated. Surfactant I is a viscous, colorless liquid; Surfactant IV is a yellowish liquid and contains a solidified portion at 23°.

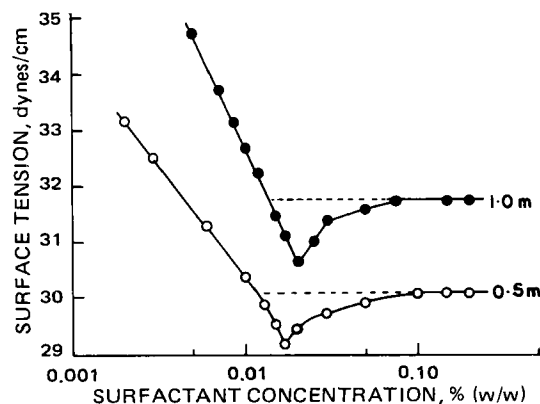
All chemicals were ACS reagent grade. The water was double distilled. The concentrations of all ternary mixtures are expressed as molality or as percent (w/w) based on the amount of water present. The preparation of ternary mixtures and the methods for assaying the electrolyte content of the concentrated stock solutions were described previously (1, 2).

Surface tensions were measured by means of a Wilhelmy balance<sup>3</sup> equipped with a thin rectangular sandblasted platinum blade which was cleaned by flaming. The receding contact angle was zero even in pure water. The solutions, stored in crystallizing dishes, had their surface cleaned by suction with a fine glass capillary. Surface tensions were measured after overnight storage at 25.0 ± 0.3°. The reproducibility of the measurements was within ±0.1 dyne/cm.

The surface tension *versus* log surfactant concentration plots for Surfactant IV in the vicinity of the CMC consisted of two straight lines, the one above the CMC being horizontal (*cf.*, Fig. 1). The CMC was taken as the intersection of these two lines, with a reproducibility of ±0.0002%. No minimum was observed down to the surfactant concentrations closest to the CMC at which surface tensions were measured, namely, 0.9 and 1.3 times the CMC of 0.055%.

The plots for Surfactant I exhibited a depression with a pronounced minimum. The flat branch rose beyond the CMC with increasing surfactant concentration and only gradually leveled off to become horizontal (*cf.*, Fig. 2). This behavior has been reported for most normally distributed polyoxyethylated octylphenols (13). The CMC was taken as the concentration corresponding to the minimum for the following reason.

The downward branch of the plots on approaching the minimum with increasing concentration was quite steep. This depression is produced by traces of highly surface-active impurities of low water solubility, presumably octylphenol molecules with zero or very few ethylene oxide units. Below the CMC, these impurities are prefer-



**Figure 2**—Effect of magnesium nitrate on the surface tension of solutions of octoxynol. Molalities (*m*) represent salt concentrations.

entially adsorbed at the air–water interface, strongly depressing the surface tension. The subsequent rise of the curve above the minimum is due to the removal of the surface-active impurities from the air–water interface into the bulk of the surfactant solution by micellar solubilization. Since the minimum corresponds to the lowest surfactant concentration at which the impurities are first solubilized by micelles, it marks the onset of micelle formation. The surfactant concentration corresponding to the minimum is, therefore, the CMC<sup>4</sup>.

While the absolute value of the CMC of Surfactant I as determined by surface tension is only approximate, relative shifts in the CMC caused by additives could be determined with a precision of about ±0.0005%.

### RESULTS AND DISCUSSION

**Effect of Additives on CMC**—The effects of electrolytes on the CMC values of the two surfactants are shown in Tables I and II. The values are expressed as percent (w/w) based on the amount of water present. The most frequently observed trend is a reduction in the CMC, which deepens with increasing electrolyte concentration. Inasmuch as the electrolytes extend the surfactant concentration range over which micelles form at the expense of nonassociated surfactant molecules, lowering of the CMC represents salting out. From an alternative viewpoint, as its solubility is lowered through salting out, a surfactant becomes more surface active and accumulates more readily at the air–water interface. Therefore, saturation adsorption and plateau surface tension are reached at lower bulk concentrations, corresponding to a reduction in the CMC. Conversely, an increase in the CMC indicates salting in.

The electrolytes most effective in lowering the CMC of the two surfactants were the nitrates of sodium and potassium. These were also the most effective cations for depressing the cloud points (1, 2). Their salting-out effectiveness becomes even more apparent when comparing electrolytes at equal ionic strengths rather than at equal molalities, because at comparable molal concentrations the ionic strength of aluminum nitrate solutions is six times greater than that of sodium nitrate while that of nitrates of divalent cations is three times greater. Even at comparable molalities, the salts of most complexing cations depressed the CMC values less than did sodium or potassium nitrate.

The CMC of Surfactant I was nearly independent of the concentrations of lithium nitrate and hydrochloric acid in most of the range of concentrations covered. Also running counter to the general trend of monotonic decreases in the CMC with increasing electrolyte concentration, the CMC of Surfactant IV was increased somewhat by

<sup>4</sup> A lower value for the CMC of Surfactant I, namely, 0.010%, would have resulted if that concentration had been determined as the intersection between the extrapolated horizontal line obtained at concentrations beyond the minimum and the inclined straight line obtained at concentrations below the CMC. The order of the electrolytes ranked according to their effect on the CMC was the same according to both graphical methods of interpolation used for determining the CMC from the surface tension–concentration plots. The order of magnitude of the changes in CMC caused by these electrolytes was also the same for both methods of determining the CMC. The electrolytes did not substantially affect the depth of the minimum, which implies that no significant association between the former and the surface-active impurities of low water solubility took place.

<sup>1</sup> Triton X-100, Rohm & Haas Co.

<sup>2</sup> Brij 96, I.C.I. America (formerly Atlas Chemical Co.)

<sup>3</sup> Rosano surface tensiometer, V.W.R. Scientific.

Table I—Effect of Additives on the CMC of Octoxynol<sup>a</sup>

Additive	CMC, % (w/w), at Additive Molalities of			
	0.50	1.0	2.0	3.0
Sodium nitrate	0.015	0.013	0.009	0.006
Lithium nitrate	0.010	0.014	0.014	0.013
Hydrochloric acid	0.015	0.014	0.014	0.014
Sulfuric acid	0.014	0.013	0.013	0.011
Magnesium nitrate	0.017	0.018	0.016	0.012
Calcium nitrate	0.012	0.013	0.009	0.007
Aluminum nitrate	0.016	0.014	0.012	0.017 <sup>b</sup>
Lead nitrate	0.015	0.013	0.010	
Nickel nitrate	0.016	0.014	0.013	0.009
Cadmium nitrate	0.021	0.020	0.022	
	<u>0.10</u>	<u>0.25</u>		
Cadmium nitrate	0.017	0.020		

<sup>a</sup>The CMC with no additive was 0.015–0.016% (w/w). <sup>b</sup>In 0.1 molal aluminum nitrate.

increasing concentrations of cadmium nitrate, following initial decreases at the lower salt concentrations.

Actual increases in the CMC values of both surfactants above their CMC values in the absence of additives were achieved by magnesium nitrate. Furthermore, cadmium nitrate increased the CMC of Surfactant I by one-third. Urea increased the CMC of Surfactant IV by as much as three-fourths above its CMC in pure water, in agreement with the observations of Schick (10) and Schick and Gilbert (11).

Lithium nitrate lowered the CMC of Surfactant IV more effectively than did sodium or potassium nitrate, in keeping with the order of the lyotropic series (4). In cloud point measurements, lithium was the only exception to the lyotropic series among the monovalent cations. Instead of lowering the cloud points more than did sodium and potassium, as expected from its position in that series, it raised them. This result was ascribed to the fact that lithium salts, unlike the salts of the other alkali metals and ammonia, form complexes with model ethers and with the ether groups of the nonionic surfactants (1, 2).

Cations bound to ether oxygens of nonionic surfactants by complexation confer a positive charge to the hydrophilic moiety. The resultant electrostatic repulsion between nonionic surfactant molecules turned cationic should increase their CMC (14). However, the very high ionic strength prevailing in the concentrated electrolyte solutions employed swamps this charge, restoring essentially nonionic conditions (15).

Most additives that depressed the CMC values brought about more extensive reductions in the CMC of Surfactant IV than in the CMC of Surfactant I, especially if the reductions are considered as a fraction of the CMC in water. This lesser salting out of Surfactant I compared to Surfactant IV may be due to the aromatic ring in the former, which, however, is unlikely to be an effective ligand in the presence of water

Table II—Effect of Additives on the CMC of Polyoxyethylated Oleyl Alcohol<sup>a</sup>

Additive	CMC, % (w/w), at Additive Molalities of			
	0.50	1.0	2.0	3.0
Sodium nitrate	0.0025	0.0025	0.0015	0.0015
Potassium nitrate	0.003	0.0015	0.0015	
Lithium nitrate	0.002	0.0015	0.001	0.0006
Hydrochloric acid	0.003	0.004	0.003	0.003
Sulfuric acid	0.005	0.004	0.003	0.003
Magnesium nitrate	0.009	0.006	0.007	0.010
Calcium nitrate	0.0065	0.004	0.005	0.004
Aluminum nitrate	0.0035	0.003	0.005	
Lead nitrate	0.0045	0.003		
Nickel nitrate	0.004	0.002	0.0025	
Urea	0.008	0.0095	0.010	0.010
Cadmium nitrate	0.0025	0.0045	0.0055	0.005
	<u>0.10</u>	<u>0.25</u>		
Cadmium nitrate	0.0025	0.003		

<sup>a</sup>The CMC with no additive was 0.0055–0.0060% (w/w).

Table III—Net Effect of Additives on the Plateau Surface Tension of Polyoxyethylated Oleyl Alcohol

Additive	$\Delta\gamma_P^a$ , dynes/cm, at Additive Molalities of			
	0.50	1.0	2.0	3.0
Hydrochloric acid	0.6	0.8	1.9	4.1 <sup>b</sup>
Sulfuric acid	0.1	–0.1	–0.5	–0.6
Magnesium nitrate	0.3	0.6	–1.7	–2.1
Calcium nitrate	0.4	–0.2	–2.3	–2.5
Aluminum nitrate	1.8	0.2	–1.9	
Nickel nitrate	0.0	–0.6	–0.6	–2.5
Urea	0.4	0.5	1.1	0.2
Cadmium nitrate	0.2	0.4	–1.0	–0.6
	<u>0.10</u>	<u>0.25</u>		
Cadmium nitrate	0.2	0.0		

<sup>a</sup> $\Delta\gamma_P$  is defined by Eq. 1. <sup>b</sup>Concentration of hydrochloric acid is 4 molal.

and ether groups. A possible alternative explanation is that Surfactants I and IV may have different polyethylene oxide chain length distributions since they were prepared by different manufacturers.

While Schick (3) reported that 0.43 M magnesium nitrate depressed the CMC of a nonoxynol containing 15 ethylene oxide units by 30% at 25°, interpolation in Table I shows that the same salt concentration raised the CMC of Surfactant I (octoxynol with 10 ethylene oxide units) by approximately 8%.

**Effect of Electrolytes on Plateau Surface Tension**—Salts that depress the CMC of nonionic surfactants were reported to lower the plateau surface tension (3, 16) or to affect it little (6). The plateau, level-off, or micellar surface tension is the surface tension at surfactant concentrations above the CMC, represented by the nearly horizontal segments in Figs. 1 and 2.

In systems comprising only polyoxyethylated surfactants and water without additives, the following two trends have been reported. Both the CMC and plateau surface tension decrease as the number of ethylene oxide units per molecule is reduced (3, 13) and as the temperature of the solution of a given surfactant is raised (3, 17). In both instances, the solubility of the surfactants is lowered: in the first, by reducing the number of ether groups per molecule; in the second, by reducing the extent of hydration of each ether group. As the bulk solubility of the surfactants is lowered, their surface activity or tendency to accumulate at the air–water interface is enhanced. Salting out by additives also represents a reduction in solubility. As was seen in the previous section, it resulted in decreased CMC values. Lowering of the plateau or micellar surface tension is also indicative of salting out by added electrolytes, whereas increases in the CMC and/or plateau surface tension by additives are indicative of salting in.

The net change in plateau surface tension of the surfactant by an additive is defined as:

$$\Delta\gamma_P = (\gamma_{PSA} - \gamma_{PS}) - (\gamma_A - \gamma^o) \quad (\text{Eq. 1})$$

where  $\gamma$  represents surface tension; the superscript *o* refers to pure water; and the subscripts *P*, *S*, and *A* refer to plateau, surfactant, and additive, respectively. The term in the first parentheses in Eq. 1 represents the effect of the additive on the surface tension of the surfactant solution. For Surfactant IV,  $\gamma_{PS} = 31.5 \pm 0.2$  dynes/cm. The term in the second parentheses of Eq. 1 corrects the first term for increases in the surface tension of water by the additive in the absence of surfactant;  $\gamma_{PSA}$  and  $\gamma_A$  were measured at identical additive molalities. Among the additives used, only hydrochloric acid lowered the surface tension of water, as reported previously (18). Urea did not change the surface tension of water substantially.

The values of  $\Delta\gamma_P$  are listed in Table III. A positive value indicates that the additive raised the surface tension of the surfactant solution more than it raised the surface tension of water. A net increase in the plateau surface tension of the surfactant solution means that the additive made it more difficult to bring a surfactant molecule from the micellar solution to the air–water interface. This suggests salting in of the surfactant by the additive, paralleling an increase in the CMC. The only exception to the foregoing is hydrochloric acid, where the positive values of  $\Delta\gamma_P$  resulted from a lowering of the surface tension of water by the additive, i.e., from negative values for  $\gamma_A - \gamma^o$ .

**Effect of Additives on Molecular Area of Surfactant Adsorbed**

**at Air-Water Interface**—The plots of surface tension *versus* the logarithm of the bulk surfactant concentration often became straight lines at concentrations as low as 10–30% of the CMC for Surfactant IV. Linear plots indicate that saturation adsorption has been reached: the surface excess concentration,  $\Gamma_2$ , of the surfactant has reached its limit and does not increase any further with increasing bulk surfactant concentration,  $C_2$ . Combining the Gibbs adsorption equation with the equation for the area,  $A$ , per surfactant molecule adsorbed at the air-water interface on the assumption of a monomolecular surfactant layer (17) gives the following expression at 25° (298°K):

$$A = -947 (d \log C_2/d\gamma) \quad (\text{Eq. 2})$$

The constant 947 is obtained by multiplying 2.303 (the conversion factor of natural to common logarithms) by the gas constant ( $R = 8.314 \times 10^7$  ergs/mole °K), by the absolute temperature (298°K), and by the conversion factor of  $10^{16}$  Å<sup>2</sup>/cm<sup>2</sup> and dividing by Avogadro's number ( $6.023 \times 10^{23}$ /mole). Solutions with a given additive level have surface tension values,  $\gamma$ , at surfactant concentrations,  $C_2$ .

The surface tension measurements were designed to determine the CMC as a function of additive concentration rather than the slope of the lines below the CMC. For most additives, the smallest number of compositions that afforded a precise determination of the CMC was studied. Despite the limited range and the paucity of  $C_2$  values employed, the following observations could be made. All additives except urea increased the negative slope  $-d\gamma/d \log C_2$  and, hence, decreased the  $A$  values. Urea produced no changes, or possibly small increases, in  $A$ . Cadmium nitrate and sulfuric acid produced the largest decreases in the area per molecule of Surfactant IV, as much as 30%, followed by hydrochloric acid and nickel nitrate. Calcium nitrate and potassium nitrate produced the smallest decreases.

These conclusions are qualitative, since the molecular areas were not always compared at saturation adsorption or at similar surface pressures. Furthermore, the area values are averages, because they depend on the chain length of the polyoxyethylene moiety (9) and the surfactant has a range of these. The average area is probably most strongly influenced by the surfactant molecules with the longest polyoxyethylene chains, which are also likely to be the most sensitive to the effect of the additives. However, the trend was general. The cross-sectional area per surfactant molecule adsorbed at the air-water interface at any specific value of surface pressure was reduced by the electrolytes; *i.e.*, the adsorbed surfactant monolayers became more closely packed. This finding is in agreement with the results of Schick (3) and Hsiao *et al.* (6). Based on a smaller number of electrolytes, which included few complexing cations, and on much more limited concentration ranges, they reported slight to moderate increases in

$-d\gamma/d \log C_2$  for all systems investigated. According to Eq. 2, this corresponds to comparable reductions in  $A$ .

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