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Effect of *n*-Alkylamine Hydrochlorides on the Cloud Point of Nonionic Polyoxyethylated Surfactant*

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Abstract—The salting in and salting out of Octoxynol, N.F., a nonionic polyoxyethylated surfactant by *n*-alkylamine hydrochlorides was investigated by measuring their effect on the cloud point of the surfactant at various salt concentrations. The carbon number of the alkyl chain was varied from zero to twelve. Ammonium chloride, methylamine hydrochloride and ethylamine hydrochloride tended to salt out the surfactant, lowering its cloud point in proportion to the salt concentration. *n*-Ankylamine and *n*-butylamine hydrochlorides showed salting-out effect at low concentrations of the electrolyte, while their effects were leveled off and showed rather salting-in trend at higher concentrations of the electrolyte. These salting-in effect was ascribed to the formation of a hydrotropy of the *n*-alkylammonium cations with the surfactant. The higher homolog compounds of *n*-alkylamine hydrochlorides showed extraordinarily high salting-in effect at very low concentrations of the electrolyte. These large salting-in effects were more drastic as the chain length was getting longer. These large increases of the cloud point of the surfactant were attributed to the formation of mixed micelles of *n*-alkylammonium cations with the polyoxyethylated surfactant.

The problem of the influence of additives on the upper consolute temperature called cloud point of nonionic polyoxyethylated surfactant in aqueous solutions is of both fundamental and applied interest. It can provide considerable information of theoretical importance as to the interactions between the components of the ternary system and the unique structure of water.

The general aspects of the salting in and salting out of nonelectrolytes by electrolytes has been extensively investigated and reviewed[1,2]. The effect of electrolytes on the activity

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of nonelectrolyte in solution is an extremely complex phenomenon; many factors are contributing diversely to the effect. These factors include the interactions between ions and nonelectrolyte, ions and solvent, nonelectrolyte and solvent, and intermolecular forces of ions, solvent and nonelectrolyte themselves. It is always partially proper to define the behavior of the nonelectrolyte in the solution with sacrifice of any factor involved.

It is generally accepted that added electrolytes hydrate water molecules, and cause electrostriction of water, and increase the internal pressure of the solution. According to Long and McDevit[1], this extra pressure increases the activity of the inert nonelectrolytes, thus causing salting out the nonelectrolytes. The salt effect usually follows the empirical equation

$$\log f = K_s C_s \tag{1}$$

where f is the activity coefficient of the nonelectrolytes in salt solution, K_s the salt-effect constant, and C_s the molar concentration of the electrolyte. Long and McDevit[3] derived an equation for K_s,

$$K_s = V_i(V_s - \bar{V}_s)/2.3\beta RT \tag{2}$$

where $\bar{V}_i$ is the partial molal volume of the nonelectrolyte, V_s the molal volume of pure electrolyte, $\bar{V}_s$ the partial molal volume of the electrolyte, and β the compressibility of water.

The effect of electrolytes on the cloud points of nonionic polyoxyethylated surfactants have been extensively studied[4~8] However, satisfactory theories predicting the effect of electrolytes on the cloud point of the surfactants are still not available, and the equation (2) was partially successful to predict the effect. Electrolytes of cations which do not form coordinate complex with ether oxygen of the polyoxyethylene moiety of the surfactants simply salt out the surfactants by competitive hydration of electrolytes and increasing the electrostriction of ths solution. However, the electrolytes with large polarizable anions such as iodide, thiocyanate and perchlorate, which are effective structure-breakers for water structure, salt in the surfactants by increased hydration of the ether groups due to the depolymerization of water structure[5,8]. The electrolytes of cations which form stable solid adduct compounds with model ether such as dioxane, cineole and ethyl ether salt in the surfactants by complex formation of the cations with the ether oxygens of the surfactant[7,8].

The author extended the effect of electrolytes on the cloud point of polyoxyethylated surfactants to the electrolytes of large cations, which might have significant effect on the water structure, employing symmetrical tetraalkylamonium halides, varying the chain length from ammonium to tetra-*n*-butylamonium halides[9]. They reported extraordinarily high salting-in effect of tetra-*n*-propyl and tetra *n*-butylamonium halides. These large salting-in effects of large symmetrical cations were not explained by the internal pressure concept and the water structure. These effects were attributed to the formation of mixed micelles of tetraalkylammonium cations with the surfactant and possibly the formation of a hydrotropy of the cations with the surfactant.

The purpose of this investigation was to extend the study of the effect of electrolytes on the cloud point of polyoxyethylated surfactants to *n*-alkylamine hydrochlorides, and to ascertain the formation of mixed micelle and hydrotropy of *n*-alkylammonium cations with the polyoxyethylated surfactant.

EXPERIMENTAL

The nonionic surfactant employed was Octoxynol N.F., a branched ocylphenol with an average of 9–10 ethylene oxide units, supplied by Rohm and Haas Co., Phila., USA. as Triton ×100. It was selected becaused it has been employed extensively in cloud point measurements. Its properties are given in ref. (8) under Surfactant I. The viscous liquid was dried over anhydrous calcium sulfate to constant weight. The *n*-alkylamine hydrochlorides were abtained from Wako Pure Chemical Co., Tokyo, Japan, and were also dried over anhydrous calcium sulfate. All other reagents were ACS reagent grade. Water was doubly distilled.

Table I—Cloud point of Octoxynol as a function of the concentration of added electrolytes[a]

Molality	NH_4Cl	$MeNH_3Cl$	$ENtH_3Cl$	*n*-$PrNH_3Cl$	*n*-$BuNH_3Cl$
0.001	64.0	63.7	63.0	62.3	62.0
0.005	63.6	63.5	62.7	62.0	62.1
0.010	63.4	63.0	62.5	61.8	62.2
0.020	63.0	62.7	61.8	62.0	62.5
0.050	62.1	62.5	61.5	62.0	63.5
0.100	60.8	61.2	60.5	62.0	63.5
0.200	60.0	59.0	60.0	61.8	65.0
0.500	56.9	55.5	57.5	61.8	71.0
1.000	52.3	50.8	54.1	62.5	81.3
1.500	48.8	48.1	50.2	64.5	92.8

[a] Concentration of Octoxynol is 1.00 % w/w based on the weight of water. Its cloud point in the absence of electrolyte is 64.3°.

Table II—Cloud point of Octoxynol as a function of added electrolytes[a]

Molality	*n*-Hexyl NH_3Cl	*n*-Octyl NH_3Cl	*n*-Decyl NH_3Cl	*n*-Lauryl NH_3Cl
0.001	64.2	64.9	75.8	91.5
0.002	65.8	68.0	83.5	b
0.005	66.3	71.8	91.0	
0.010	68.2	77.0	b	
0.020	72.1	95.0		
0.050	79.8	b		
0.100	85.7			
0.200	94.5			
0.300	b			

a Concentration of Octoxynol is 1.00% based on the weight of water.

b The cloud point is over 97°.

The procedure for preparing the ternary electrolyte–surfactant water mixtures and for measuring cloud points are described in Ref. (7). The surfactant concentration was 1.00% w/w based on the amount of water present. Electrolyte concentrations are expressed as molality (m) based on the amount of water present in the mixtures.

RESULTS

The cloud point of 1% Octoxynol, N.F. aqueous solutions in the presence of ammonium chloride and various *n*-alkylamine hydrochlorides is listed in Table I and II. The behavior of electrolytes underwent profound changes as the number of carbon atoms per akly group was increased from zero to twelve. Ammonium chloride, methylamine hydrochloride and ethylamine hydrochloride produced moderate decreases in cloud point, and the tendency to lower the cloud point of the surfactant became stronger with increasing concentration of the electrolyte. Methylamine hydrochloride had the strongest salting-in efficiency, lowering the cloud point by more than 13° at the 1 molal level. *n*-Propyl and *n*-butylamine hydrochlorides showed salting-out effects at moderate concentration of the electrolyte. However, these effects were leveled off at 1.500 molal concentration of *n*-propylamine hydrochloride and 0.200 molal of *n*-butylamine hydrochloride, and they showed rather salting-in effects at higher concentration of the electrolyte. As the alkyl group was increased to *n*-hexyl and higher homologs, the salting-out effects disappeared, and the salting-in effects become very pronounced at low concentration of the electrolyte. The salt effect of the *n*-alkylamine hydrochlorides as a function of the number *P* of carbon atoms of alkyl group at 0.010 molal concentration of the electrolyte is also illustrated in Fig. 1. The compounds with carbon number from zero to four decreased the cloud point, and the higher homologs increased the cloud point drastically as the carbon number increases. The curve has a minimum for $P=3$.

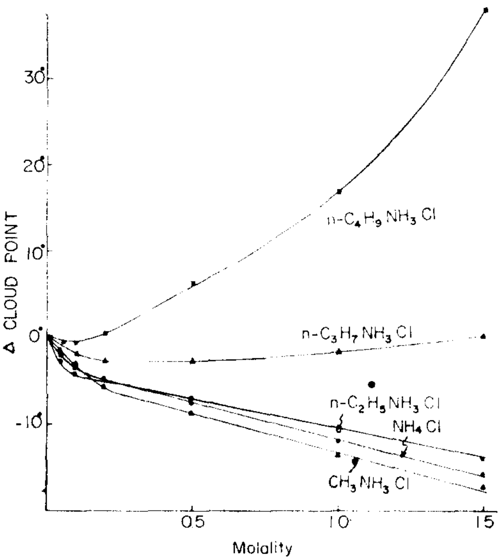

Fig. 1—Effect of chain length of the *n*-alkylamine hydrochlorides on cloud point of Octoxynol at 0.010-m electrolyte concentration; P=number of carbon atoms per alkyl group.

DISCUSSION AND CONCLUSION

The influence of the chain length of the alkyl group on the nature and magnitude of the salt effect of the *n*-alkylamine hydrochlorides must be attributed to more than one factor because the effect changes from salting out for lower homologs to salting-in for higher homologs. Attempts to explain these observations in terms of current theories of salt effect and water structure are made below.

Long and McDevit derived the equation (2) which explains the effect of electrolytes on the activity coefficient of nonelectrolytes in terms of internal pressure[1]. The difference $(V_s - \bar{V}_s)$ represent the extent of electrostriction of water by the electrolyte. Although these data for *n*-alkylamine hydrochlorides are not available, it is evident to see that the electrostriction effect should not be so large to explain the profound salting-in effect of the electrolyte as the length of alkyl chain is longer than *n*-hexyl at such a low concentration at 0.010 molal. At this level of concentration the electrostriction effect should be minor. Thus the internal pressure theory does not apply to the present situation in explaining the salt effect.

As explained in the case of tetra-*n*-alkylammonium halides[9], the hydrophobic hydrocarbon chain of the *n*-alkylamine hydrochlorides must enhance the structure of water; the larger the alkyl group, the greater this effect[10]. These hydrophobic groups do not attract or orient the water molecules in their immediate vicinity as strongly as does the next shell of water molecules, which surrounds the water molecules nearest to the hydrocarbon groups. Thus, the nearest water molecules are oriented and hydrogen bonded more strongly to the water molecules beyond them than would be the case if there were a strong counter-attraction from the side of hydrocarbon groups. This produces a tighening of the structure of the water surrounding the groups. As structure makers, *n*-alkylamine hydrochlorides enhance the association among water molecules, and consequently should salt out the surfactants. The observed profound salting-in effect produced by higher homologs of the *n*-alkylamine hydrochlorides are in direct opposition to their structure-making activity. This discrepancy may be ascribed to the structure-breaking effect of temperature. At the cloud point temperature and higher, the icebergs" or "flickering cluster" [11] are probably largely melted or broken up. Another strong possibility is that in the effect of the *n*-alkylamine hydrochlorides, the effect of the electrolyte on the water structure is minor comparing with the effect such as association of the cations with the cations with the surfactant.

It has been known that *n*-alkylamine hydrochlorides associate in aqueous solution by micelle formation[12], and there is a very strong likelihood that Octoxynol and the alkylamine hydrochlorides form mixed micelles since the critical micelle concentration of the surfactant is far below the 1.00% use level even at room temperature. Nonionic surfactants have a pronounced tendency to form mixed micelles with anionic[13] and cationic[14] surfactants. The cloud point of the nonionic surfactants are considerably raised by comicellization[5,15]. Of the nine chlorides examined, ammonium chloride, methylamine, *n*-propylamine and *n*-butylamine hydrochlorides are unlikely to associate into comicells because they showed salting-out effect at moderate concentration of electrolyte. The salting-in effect that *n*-propylamine and *n*-butylamine hydrochlorides showed at higher concentration of electrolyte should be ascribed to the formation of a hydrotropy of the cations with the surfactant, of which phenomenon is described well in ref. (16). For *n*-hexylamine and higher homologs of *n*-alkylamine hydrochlorides, the hydrocarbon chain is long enough to be hydrophobic and to have the tendency toward forming micelles by themselves or mixed micelles with Octoxynol.

From above discussion, it is appropriate to ascribe the large salting-in effect of *n*-hexylamine and higher homolgs of *n*-alkylamine hydrochlorides to the formation of mixed micelles of the cations with the nonionic polyoxyethylated surfactant.

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