Electrolyte Effects on Micellar Solutions of Nonionic Detergents

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The effect of electrolytes upon aqueous solutions of nonionic detergents is studied by examining the distribution of the three components between the conjugate phases in the corresponding ternary diagrams. NaSCN and NaCl are chosen as examples of salts producing an increase and a decrease in the cloud points of detergent solutions.

The results are discussed by treating the salt effects as similar to the effect of added solvents or nonsolvents upon the miscibility of polymer solutions. With the use of Scott's "single liquid" approximation, values for the interaction parameter of polymer theories are obtained.

INTRODUCTION

Solutions of nonionic detergents of the polyoxyethylene type in water separate out in two liquid phases on raising the temperature. The temperature at which phase separation takes place, or cloud point, is dependent on the detergent concentration, thus giving rise to binary phase diagrams which may be described using the theories of polymer solutions (1). Measurements of heats and entropies of mixing for these systems (2.3) have yielded information concerning the deviations from ideal behavior which give rise to lower consolute temperatures.

The addition of electrolytes to these micellar solutions results in alterations in the clouding temperatures, which have been studied mainly in connection with the effect of the type of electrolyte on detergent solutions at a fixed, dilute concentration (4.5). In order to get a better understanding of the changes produced by the addition of electrolyte, it appears of interest to study the composition of both conjugate phases with and without added salts; this is done in the present work for a wide range of detergent concentrations. The results of such measurements are presented together with a treatment based on the theories of polymer solutions (6.7). It is hoped that along these lines the relation between the salt effects on the critical micelle concentration and on the clouding temperature (8) may be further clarified.

EXPERIMENTAL

1. *Materials* Samples of octylphenylpolyethoxyethanol used as the nonionic detergent were supplied by Rohm and Haas Co., Philadelphia (trade name Triton X114). The samples were purified and analyzed as described elsewhere (1); the number average of ethyleneoxide units in the chain came out as 7.3 EO per molecule. The salts used were of Analar Grade; water was tridistilled from Pyrex stills prior to use.

2. *Experimental Methods.* Cloud points were determined visually as previously described (1); the detergent concentration was varied between 0.5% and 40%; the influence of salts upon the cloud points was tested.

Detergent concentrations were determined by measuring the optical density at

277 millimicrons with a Perkin Elmer Spectrophotometer, type 202.

Electrolyte concentrations were determined by analyzing the sodium present with a Perkin Elmer Atomic Absorption set, type 303.

The compositions of the conjugate phases at equilibrium were obtained by placing solutions of known total composition in glass-stoppered tubes immersed in a water bath at 40°C ± 0.02°. The samples were kept in the bath for 30 hours with occasional shaking. After this time, samples of the upper (α) and lower phases (β) were isolated, and the salt and detergent concentrations in a given phase were measured as described above.

The binodial curves of the ternary diagrams were obtained from the data of direct analysis of detergent and salt for the case of the dilute branch of the diagrams. The points for the solutions more concentrated in detergent were obtained by interpolation at 40°C in the curves shown in Fig. 3. The tie lines of the ternary diagrams were obtained by joining the corresponding electrolyte concentration in both phases.

3. *Results*. The ternary diagrams for the systems water-detergent-salt for both NaCl and NaSCN are presented in Fig. 1. The diagrams cover detergent and electrolyte concentrations up to 32% and 4%, respectively; because of this, the diagram has not been drawn as an equilateral triangle but as an isosceles one (9).

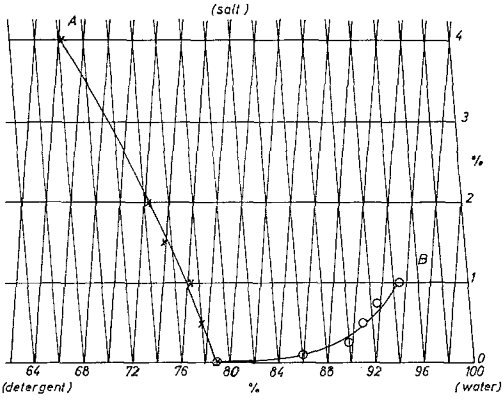

FIG. 1. Ternary diagrams water-detergent-electrolyte. Curve *A*. Water-detergent-NaCl. Curve *B*. Water-detergent-NaSCN.

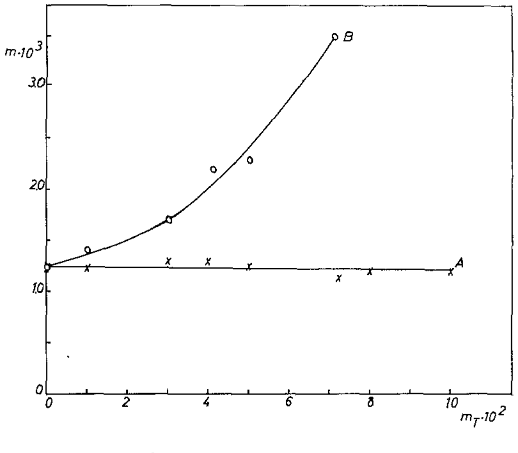

FIG. 2. Variation of the concentration (molal) of detergent in the "dilute phase" with the molality of added electrolyte. Curve *A*: NaCl added. Curve *B*: NaSCN added.

The influence of electrolyte concentration on the amount of detergent present at equilibrium in the dilute phase at 40°C is represented in Fig. 2; for both salts the detergent concentrations are so small that they would appear coincident with the right branch of the triangle of Fig. 1.

The cloud temperatures of the detergent solutions with added salt at varying detergent concentrations are shown in Fig. 3.

The concentrations of electrolyte in both the dilute and concentration phases are presented in Fig. 4. The distribution coefficients of both salts between the two conjugate phases correspond to the slopes of the lines *A* and *B*.

DISCUSSION

As stated in the Introduction, it appears convenient to study in detail the influence of added NaCl and NaSCN on an aqueous detergent solution; these salts are taken as examples of electrolytes producing opposite effects, namely, salting out and salting in, respectively.

The influence of both electrolytes on the cloud points of the micellar solutions may be

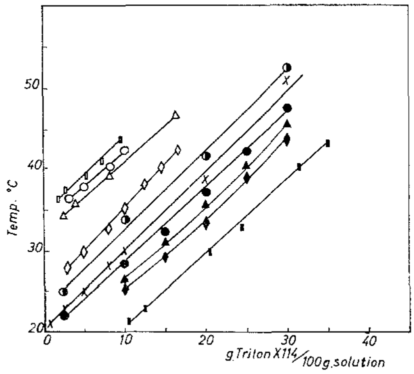

FIG. 3. Cloud points of the ternary solutions as a function of the total concentration of detergent. Without added electrolyte, ×. NaI added, 0.0335 molal, ◑. NaSCN added, 0.0123 molal, ◇. NaSCN added, 0.0619 molal, △. NaSCN added, 0.0931 molal, ○. NaSCN added, 0.1245 molal, ▯. NaCl added, 0.129 molal, ●. NaCl added, 0.26 molal, ▲. NaCl added, 0.349 molal, ◆. NaCl added, 0.713 molal, ▮.

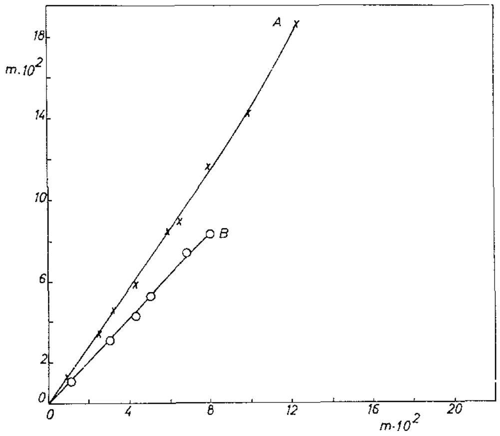

FIG. 4. Concentration (molal) of electrolyte in the "dilute phase" as a function of the concentration (molal) of electrolyte in the conjugated "concentrated phase". Curve A: NaCl. Curve B: NaSCN.

visualized from the corresponding ternary diagrams, presented in Fig. 1. By comparing curves A and B in that figure it may be seen that an increase in electrolyte concentration produces a lowering of the miscibility in the case of the chloride and a rise of the miscibility in the case of thiocyanate.

On the ternary diagrams of Fig. 1, only that consolate phase which is more concentrated in detergent (β) is represented; this is because the region of the binodial curve corresponding to the more dilute phase (α) is coincident with one of the sides of the triangle. In order to visualize the effects of both electrolytes on the dilute phase, the concentrations of detergent in that phase are represented as a function of electrolyte concentration in Fig 2. The slight decrease in detergent concentration observed in the case of NaCl is in agreement with the small dehydrating effect induced on the consolute phase concentrated in detergent, which is apparent in Fig. 3 from the displacement of the curves towards regions of lower water concentration. On the other hand, in the case of added thiocyanate a marked increase in the equilibrium concentration of detergent in the "dilute phase" may be observed; this effect, together with the increase in water content of the concentrated phase, illustrates the enhanced miscibility referred to above.

The simultaneous effect of the main variables concerned, i.e., temperature, concentration of detergent, and concentration and type of added electrolyte, on the phase separation of these micellar solutions may be described by Fig. 3. There, the results at various temperatures are represented as conventional binary diagrams, each curve corresponding to the same concentration of electrolyte. The use of binary diagrams for three-component systems may be justified (a) when the concentration of the third component is low and (b) when the composition of the "mixed solvent" (i.e., water and electrolyte) thus formed is the same in both phases. The last requirement is equivalent to using Scott's "single liquid" approximation (7), which will be discussed later.

It may be observed from Fig. 3 that an increase in NaCl concentration at a fixed temperature results in a decrease in the water concentration in the concentrated phase; the same effect is obtained when the temperature is raised at constant total ϕ_2; this implies that addition of given amounts of NaCl may be related to corresponding temperature increments, whereas the addition of NaSCN may be related to a temperature decrease.

It also may be seen from the results of Figs. 1 and 3 that when an electrolyte lowers the cloud point it will do so because of a dehydrating effect on the concentrated phase; smaller or larger depressions of the cloud points will then be related to corresponding smaller or greater increases in detergent content of the concentrated phase. The opposite effect will be the case for electrolytes that increase the cloud point (SCN^-, I^-, ClO_4^-). The usual graphs, which present the effect of electrolytes upon the cloud point for a fixed detergent concentration (4.5) may be obtained from the curves of Fig. 3 by noting the points obtained by a vertical displacement along the temperature axis at a fixed detergent concentration.

DISTRIBUTION OF SALTS BETWEEN THE CONJUGATE PHASES

The above-mentioned effect of electrolyte on the miscibility may be related to the distribution coefficient of the salts between the conjugate phases (10). From the straight-line relationships shown in Fig. 4, a single distribution coefficient of 1.47 is obtained for NaCl, and 1.04 for NaSCN. These are obtained from the ratio of weight concentration of the electrolyte in the aqueous phase over that of the concentrated phase. These values obtained are in qualitative agreement with empirical rules (10) about the effect of a third substance on the miscibility of liquid pairs.

The fact that the distribution coefficients of both salts seem to be independent of the salt concentration in the range examined is likely to be fortuitous. This is apparent from a thermodynamic definition of distribution coefficients of electrolytes, namely,

$$RT \ln \left(\frac{c_3^{\alpha}}{c_3^{\beta}}\right) = RT \ln K_{\frac{\alpha}{\beta}} = \mu_3^{0\beta} - \mu_3^{0\alpha} + RT \ln \frac{\gamma_{3\pm}^{\beta}}{\gamma_{3\pm}^{\alpha}}, \quad [1]$$

where the μ_3^0 stand for the molar free energies of component 3 at unit molality, c_3 for the molalities, and γ_3 for the activity coefficients. Since in the present case the composition of the phases changes with the addition of electrolyte, the μ_3^0 terms are bound to be different for each point, so that even if the mean activity coefficients of the salts were concentration independent, the concentration ratio should not be a constant.

The concentrated phase is made up of micelles dispersed in the salt solution; the distribution coefficients may then be recalculated on the assumption that no electrolyte is present in the interior of the micelles. This amounts to defining distribution coefficients as the ratios of electrolyte concentrations in the water present in both phases, and to assuming that the micelles would merely provide an excluded volume for the ions in which the distribution coefficients should be 1.00. Such a calculation gives $K^*_{\alpha/\beta} = 1.13$ for NaCl and 0.95 for NaSCN; the values obtained are not very different from unity, so that the above assumption may be taken as approximately correct. The implication of these values will be discussed more fully in the following section.

APPLICATION OF THE EQUATIONS OF POLYMER SOLUTION THEORY

The electrolyte effects on the miscibility of the detergent-water liquid pair may be discussed along the same lines as the nonsolvent effects on a polymer solution. The application of the Huggins theory of polymer solutions to binary water-detergent systems has been discussed in a previous work (1). It was concluded there that a phase separation in micellar systems could be described through the equation:

$$\ln \phi_1^c + \ln \phi_2^c + \chi(\phi_2^c)^2 = 0, \qquad [2]$$

In Eq. [2] the subscripts 1 and 2 stand for the solvent and the detergent, respectively, ϕ_i^c are the volume fractions of each species for which phase separation occurs, and χ is an "interaction parameter" fully discussed in reference 1.

The addition of electrolyte changes the system into a ternary one; however, the system is strictly a multicomponent one since the detergent is a mixture of homologs of varying chain lengths. The pertinent equations for phase separation in multicomponent systems have recently been developed by Koningsveld *et al.* (11), but in their present form they are not applicable to the system discussed here since the molecular weight distribution is unknown.

As a preliminary treatment the detergent will be considered as a single molecular species and the electrolyte solution will be treated using the "single liquid approximation" of Scott (7); that is, the ternary system will be treated as a binary solution so that the mixed solvent is considered as a single one. On the basis of Scott's treatment the "single liquid approximation" will be justified when the composition of the mixed solvent is the same in both phases. Since the values found for the distribution coefficients calculated by neglecting the detergent volume are not very different from 1, that is, 1.13 and 0.95, the use of Scott's approximation may be justified here.

Under the approximation discussed, the chemical potential of the "single solvent" may be written as:

$$\frac{\Delta\mu_1}{RT} = \ln \phi_1 + \phi_2 + \chi\phi_2^2. \qquad [3]$$

In Eq. [3] the scripts 1 and 2 refer to the "single solvent" and the detergent, respectively, $\Delta\mu_1$ being the difference between the chemical potential of the single solvent (μ_1) in the solution and that of the pure single solvent (μ_1^0) at temperature T.

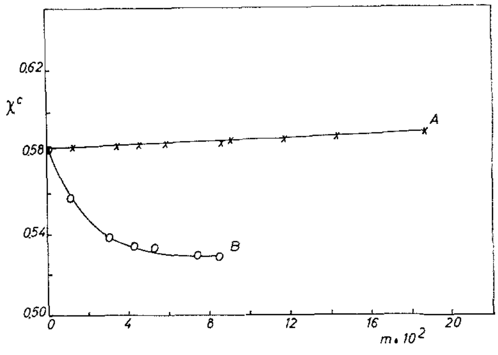

FIG. 5. The interaction parameter χ^c as a function of salt concentration (molal). Curve A: NaCl. Curve B: NaSCN.

Applying the same phase separation criteria as that used for binary systems (1), namely, $\mu_1^\alpha = \mu_1^0$, the left-hand side term of Eq. [3] is zero. Thus, the values of the interaction parameter χ^c may be calculated using Eq. [2], provided the values of the critical volume fractions of detergent are known from experiment. The values of χ^c thus calculated are presented in Fig. 5 as a function of electrolyte concentration in the "dilute phase" (Curve A). For the case of NaSCN, the concentration of detergent in the "dilute phase" should not be neglected (see Fig. 2), so that a more extended equation (7) should be used in place of Eq. [2], namely,

$$\chi^c = \left[\ln \frac{(1-\phi_2)^\beta}{(1-\phi_2)^\alpha} + \phi_2^\beta - \phi_2^\alpha\right] \cdot \frac{1}{(\phi_2^\alpha)^2 - (\phi_2^\beta)^2}\,. \qquad [4]$$

The values calculated for the case of added NaSCN are shown on Curve B of Fig. 5. These values may be compared with those obtained from measurements of water vapor pressures in homogeneous solutions of the same detergent without added electrolyte (1); if this is done, the addition of NaCl or NaSCN may be described through an increase or a decrease in χ respectively.

The opposite effects of both salts on the interaction parameter may be related to the effect of electrolytes on the heats of solution. A number of results (12.13) point to a decrease of the heat of solution of a nonelectrolyte in water when salts such as chlorides or sulfates are added. For salts like thiocyanates or iodides, which produce an increase in miscibility, the opposite effect may be predicted.

Preliminary measurements of the heats of mixture of Triton X-100 in solutions of Na_2SO_4 and NaSCN provide values of 1.4 and 0.8 for the ratios of the heats of solution H_2O/Na_2SO_4 and H_2O/NaSCN, respectively.

The value of the interaction parameter may be expressed as the sum of two terms (6), including the enthalpic (χ_n) and entropic (χ_s) contributions:

$$\chi = \chi_n + \chi_s, \qquad [5]$$

where

$$\chi_n = \frac{\overline{\Delta H_1}}{RT\phi_2^2}, \qquad [6]$$

ΔH_1 being the partial molar enthalpy of the solvent minus the molar enthalpy of pure solvent.

Since for these systems χ_n appears to be negative (1), a decrease in χ_n will produce an increase in χ, and hence the miscibility range will be narrowed; this is in agreement with the effect found upon addition of sulfates and chlorides.

The above preliminary treatment follows the same lines as the general one that may be used to describe the effects of any other co-solvent which alter the miscibility. Such would be the case, for example, of the addition of ethanol to H_2O-detergents mixtures (8).

It is worthy of comment that the effect of electrolytes on the cloud points of polyethyleneglycols is strikingly similar to the one noted for nonionic detergents (14). This, coupled with the similarity of the excess thermodynamic functions for both types of substances (1, 2), may be taken as evidence that the effect of the electrolyte upon the miscibility is exerted at the level of the polyoxyethylene chains, the hydrocarbon segments merely providing an excluded volume for the solvent. Work along these lines is currently being pursued.

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