THERMODYNAMIC BEHAVIOR OF SODIUM DEOXYCHOLATE, SODIUM DODECYL-
SULPHATE AND SODIUM TETRADECYLSULPHATE MICELLAR SOLUTIONS

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In this paper we have studied the thermodynamic behavior in aqueous solution of three anionic surfactants: Sodium dodecylsulfate (SDS), sodium tetradecylsulfate (STS and sodium deoxycholate (SDC). From osmotic pressure data and theoretical association models we have calculated several excess functions ($S^E$, $G^E$ and $H^E$) in the temperature range 298-363 K.

Also we have calculated dimerization and multimerization constants and association numbers of the three surfactants at all measured temperatures. The values obtained are in accord with those calculated from other experimental techniques.

INTRODUCTION

Nowadays, thanks to the development of electronics, it is possible to obtain high sensitivity vapor pressure osmometer. This offers new possibilities for the thermodynamic study of systems which cannot be studied by any other physical method. In the last ten years, vapor pressure osmometry (VPO) has been increasingly applied in the determination, not only of molecular weights, but also of dissociation constants of acids and bases, activity and osmotic coefficients of electrolytes and non-electrolytes, and excess properties. This technique allows the calculation of these parameters with relative ease and efficiency.
Moreover, through the use of several mathematical models and experimental data, the association mechanism of a micellar system can be determined, as well as the parameters associated with the process.

In this paper, several excess thermodynamic functions (excess free Gibbs energy, $G^E$, excess enthalpy, $H^E$, and excess entropy, $S^E$) as a function of surfactant concentration and temperature (in the range 298-363 K) have been calculated. Using several mathematical models we have determined the type of association of the three detergents studied (Sodium Deoxycholate, Sodium Dodecylsulphate and Sodium Tetradecylsulphate). Finally, self-association constants have been calculated for the different association models.

**EXPERIMENTAL**

Sodium deoxycholate, sodium dodecylsulphate and sodium tetradecylsulphate were purified by standard procedures.

The osmometry measurements were carried out on a Knauer 1974 model vapor pressure osmometer in the temperature range 298-363 K. Calibration of the probe, containing two thermistors, was made using aqueous solutions of sodium chloride of well known activity coefficients as standards, which are expressed as a function of molality

$$\ln \gamma = -A\sqrt{m}/(1 + B\sqrt{m}) + Cm + Dm^2$$

where $A$ is the theoretical Debye-Huckel coefficient. The other coefficients are determined by the trial and error method.

The $\Delta R$ values for both the standard and the solutions were recorded on a Houston Recorder as a function of time. In all the samples 2-3 min. were enough to attain constant resistance. At least three $\Delta R$ values were measured for each solution and the mean value was taken. The drop size was kept as constant as possible and equal in the two thermistors, so that the precision of the $\Delta R$ values ranged between 0.5 and 1.0 per cent.

The osmotic coefficients of sodium chloride were calculated from the expression

$$\phi = 1 - (A/B^3m)[1 + B\sqrt{m} - 1/(1 + B\sqrt{m}) - 2\ln(1 + B\sqrt{m})] + Cm/2 + 2Dm^2/3$$

and the osmotic or experimental molality is calculated from the relation

$$\bar{m} = \nu m\phi$$

where $\nu$ is the total number of ions in solution and $m$ is the stoichiometric theoretical molality. On the other hand, we have

$$\phi = 1 + \sum_{x=1}^{n} a_x x^x$$

where $a_x$ is the coefficient of the polynomial which better adjusts to the previous equation. The criterion of the appropriate degree of the polynomial was the minimum standard deviation of the recalculated osmotic coefficients values.