The Aggregation of Span 80 in Toluene

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The aggregation equilibria of the non-ionic surfactant Span 80 in toluene has been studied by vapour pressure osmometry (VPO) at different temperatures. The experimental data, treated both graphically and numerically using the LETAGROP-SUMPA program, can be explained by assuming the formation of dimers. The thermodynamics of Span 80 in toluene have also been calculated from the van't Hoff equation.

KEY WORDS: Aggregation equilibria, sorbitan monooleate, Span 80, vapour pressure osmometry.

1. Introduction

Sorbitan monooleate (Span 80) is the non-ionic surfactant most frequently used in metal extraction with emulsion liquid membranes. In this technique the extractant forms an organic film separating the two aqueous phases (the feed and the strip solutions) and the surfactant is used to stabilize the emulsion.

In order to study the role of the surfactants in the extraction of metals it is necessary to elucidate, as a first step, the interaction of the extractants with the organic solvent used. The study of the aggregation equilibria in organic solvents is essential in order to ascertain the stoichiometry of the extracted species and their corresponding equilibrium constants in systems involving extractant reagents.

In order to elucidate the aggregation phenomena in organic solutions several experimental techniques have been used: IR spectrometry, light scattering, viscosimetry, conductometry and osmometry, with osmometry the most conclusive. Several research workers have used osmometric measurements to determine mean aggregation numbers and aggregation equilibrium constants.

Osmometry involves the measurement of the difference in resistance $\Delta R$ between two thermistors one containing a drop of pure solvent

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and the other a drop of solution. Since the measured $\Delta R$ is directly proportional to the difference of temperature between the thermistors it is also a function of the difference in vapor pressure $\Delta p$ of the two drops, and so it is directly related to the solute molality. The theoretical relationships between $\Delta R$ and $\Delta p$ are well described by Paatero\(^6\).

Although Span 80 is known to form aggregates in organic solvents the mean aggregation number varies from 2 to 29. These spread values found in the literature\(^8\) for the aggregation number of Span 80 are mainly attributed to the nature of the organic solvents used, 29 in benzene, 26 in cyclohexane, 12 in carbon tetrachloride and 2 in chloroform. No data have been found for the aggregation of Span 80 in toluene.

It has been reported that the extraction of copper by LIX 65N\(^{14}\) or trilaurylammonium chloride (TLAHC\(_1\))\(^{15}\) decreases with increasing Span 80 concentration, suggesting the formation of complexes between extractant and Span 80. On the other hand the formation of dimers of Span 80 has been suggested\(^15\) in the data treatment by TLAHC\(_1\) of copper extraction from chloride solutions in the presence of Span 80 in toluene.

As a first step in the thermodynamic treatment of metal extraction data when using Span 80 as emulsifier, the aggregation equilibria of Span 80 in toluene have been studied by vapor pressure osmometry and is presented in this work. The influence of temperature on the aggregation equilibria has also been considered.

### 2. Experimental

#### 2.1. Reagents and Solutions

Sorbitan monooleate, Span 80, (Sigma) and toluene (Riedel-de Haën, p.a.), were used without further purification. Benzil (Merck, p.a.) was twice recrystallized from dried methanol.

Solutions of Span 80 in toluene were prepared by weight. A molality concentration range from 0.020 up to 0.260 mol-kg\(^{-1}\) was covered.

#### 2.2. Experimental Technique

The osmometric measurements were carried out using a Knauer vapor pressure osmometer with an universal probe which had been previously calibrated with benzil in toluene. Benzil was used as standard because is expected to be monomeric in toluene under the experimental conditions used.\(^{16}\)

In order to obtain reliable $\Delta R$ values and since there is a time