From the Pharmacy Department, University of Manchester, Manchester (U.K.)

The solution properties of some nonionic surface-active agents in non-aqueous solvents

By D. Attwood, C. E. Jagielski, C. McDonald, and A. E. Wilkinson

With 5 figures and 4 tables

(Received November 6, 1973)

Introduction

In a previous paper we have determined the degree of aggregation of a series of commercial polyoxyethylene sorbitan fatty acid esters (Tweens) and sorbitan fatty acid esters (Spans) in benzene (1). Solutions of all of the detergents under investigation were observed to fluoresce when excited with light of wavelength 436 nm. It was shown that failure to correct for the contribution of the fluorescence to the scattered light resulted in a considerable overestimation of the extent of aggregation. Of the detergents studied, only sorbitan monooleate (Span 80) was shown to aggregate to any significant extent in benzene and a mean aggregation number of 29 monomers was calculated.

In the present investigation we have determined the state of aggregation of selected Tweens and Spans in cyclohexane, carbon tetrachloride and chloroform. The results are discussed with reference to the solubility parameters of the solvents.

Experimental

Materials

Commercial samples (Honeywill-Atlas Ltd.) of polyoxyethylene (20) sorbitan monolaurate (Tween 20); polyoxyethylene (20) sorbitan monooleate (Tween 80); sorbitan tristearate (Span 65) and sorbitan monooleate (Span 80) were purified by repeated refluxing with a mixture of ethylene dichloride and water. The purified detergent was recovered from the ethylene dichloride by evaporation and subsequently dried under vacuum at 60°C. Solvents were fractionally distilled and thoroughly dried over calcium chloride. To avoid any possible batch variation, the same sample of each detergent was used throughout.

Light-scattering measurements

Measurements were made at 35°C with a Fica 42000 photogoniodiffusometer (A.R.L. Ltd.) using incident wavelengths of 436 and 546 nm. Solutions were repeatedly clarified by filtration through 0.1 μm millipore filters until a dissymmetry ratio for the light-scattering at 30 and 150° of less than 1.01 was achieved. Refractive index increments, dn/dc, were measured at 436 and 546 nm using a differential refractometer, calibrated with aqueous potassium chloride solutions.

Sedimentation velocity measurements

Sedimentation studies were carried out on solutions of Span 80 in each of the solvents using a Beckman Model E Analytical Ultracentrifuge with schlieren optics. All determinations were carried out at 20°C with a rotor speed of 56100 rev min⁻¹ and diaphragm angles of 65°–75°. 12 mm capillary and valve type synthetic boundary cells were used with carbon tetrachloride and cyclohexane. Chloroform, however, caused excessive softening of the materials of these cells and consequently 12 mm single sector cells (4° sector angle) with aluminium centrepieces were used with this solvent. Photographs were taken at intervals of 4 or 8 min on Ilford G. 30 plates.

Vapour pressure osmometry

Measurements were made at 35°C using a Hewlett-Packard 302 vapour pressure osmometer, calibrated with naphthalene for each of the solvents. The molecular weight was calculated from the intercept of plots of V/c against concentration, c, where V is the bridge output voltage.

Density measurements

The partial specific volume, V, of Span 80 in each solvent was calculated from

\[ \bar{\rho} = \rho_0 + (1 - \bar{\rho}_0) c. \]  \[1\]

The densities of the pure solvents, ρ₀, and of the Span 80 solutions, were determined using a 10 ml Lipkin pycnometer.
Measurement of fluorescence

A Baird Atomic Fluorispec SF100E was used to determine the fluorescent spectra emitted when detergent solutions were excited with incident light of wavelengths 436 and 546 nm.

Results

The concentration dependence of the light-scattering at 90° in excess of the solvent scatter, \( \Delta S_{90} \), for Span 80 in each of the solvents is shown in fig. 1. Similar differences in the magnitude of the scattering at 436 and 546 nm were observed for the remaining detergents in each solvent. The apparent molecular weights calculated at each wavelength are given in table 1. An examination of the fluorescent emission spectra from 5% solutions of each detergent revealed considerable fluorescence when solutions were excited at a wavelength of 436 nm, but little, if any, fluorescence when excited at 546 nm (see fig. 2). It is this difference in the fluorescent intensity at the two wavelengths which is responsible for the corresponding differences in the intensity of the light-scattering.

The light-scattering data were corrected for the errors arising from acceptance of the fluorescent light, using a method proposed by Tuzar and Kratochvil (2). Assuming non-polarisation of fluorescent radiation at all angles, the intensity of Rayleigh scattering, \( I_0 \), from a system of small isotropic particles at an angle, \( \theta \), was calculated from

\[
I_0 = \frac{2}{\pi^3} \frac{\sin \theta}{(1 + \cos^2 \theta)} \cot \theta.
\]

\( I_0 \) is the total measured intensity of the light emitted at an angle \( \theta \) and \( \alpha_0 \) denotes the ratio, \( \sin \theta/(1 + \cos^2 \theta) \). The concentration dependence of \( I_0 \) is shown in fig. 3. Aggregation numbers were calculated from the values of \( I_0 \) in the usual manner and are summarised in table 2. The quoted confidence limits (\( P = 0.95 \)) are

![Fig. 1. Plots of uncorrected scattering ratio at 90°(\( \Delta S_{90} \)), as a function of concentration, for Span 80 in non-aqueous solvents. Upper lines refer to an incident wavelength of 436 nm; lower lines refer to wavelength of 546 nm.](image-url)

Table 1. Apparent molecular weights of Tweens and Spans from light-scattering and vapour pressure osmometry

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Nominal mol.wt. ( \times 10^{-3} )</th>
<th>Mol.wt. from osmometry ( \times 10^{-3} )</th>
<th>436 nm</th>
<th>546 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tween 20</td>
<td>CCl(_4)</td>
<td>1.23</td>
<td>0.97</td>
<td>0.0135</td>
</tr>
<tr>
<td></td>
<td>CHCl(_3)</td>
<td>1.23</td>
<td>0.87</td>
<td>0.0377</td>
</tr>
<tr>
<td>Tween 80</td>
<td>CCl(_4)</td>
<td>1.31</td>
<td>1.00</td>
<td>0.0184</td>
</tr>
<tr>
<td></td>
<td>CHCl(_3)</td>
<td>1.31</td>
<td>1.09</td>
<td>0.0393</td>
</tr>
<tr>
<td>Tween 60</td>
<td>CCl(_4)</td>
<td>0.96</td>
<td>0.77</td>
<td>0.0050</td>
</tr>
<tr>
<td></td>
<td>CHCl(_3)</td>
<td>0.96</td>
<td>1.90</td>
<td>0.0163</td>
</tr>
<tr>
<td></td>
<td>C(_6)H(_12)</td>
<td>0.96</td>
<td>0.99</td>
<td>0.0330</td>
</tr>
<tr>
<td>Tween 80</td>
<td>CCl(_4)</td>
<td>0.43</td>
<td>0.50(^a)</td>
<td>0.0181</td>
</tr>
<tr>
<td></td>
<td>CHCl(_3)</td>
<td>0.43</td>
<td>0.42</td>
<td>0.0388</td>
</tr>
<tr>
<td></td>
<td>C(_6)H(_12)</td>
<td>0.43</td>
<td>0.52(^a)</td>
<td>0.0495</td>
</tr>
</tbody>
</table>

\(^a\) System showed a concentration dependent increase in mol.wt.