A commercially important polyelectrolyte, xanthan, was chosen for a systematic analysis of the relationship between molecular conformation and surface properties. In the first study the effects of ionic strength, xanthan concentration and temperature on the xanthan molecular conformation were investigated by potentiometric titration. The effects of the same factors and of the degree of ionization on the surface tension of xanthan solutions were then analyzed by the drop weight and the Wilhelmy plate methods.

Potentiometric titration studies showed that the ordered xanthan conformation is stabilized mainly by hydrogen-bonds which can be disrupted by increasing the electrostatic potential of the molecule.
or by increasing the solution temperature. Adding salt or increasing the xanthan concentration did not affect the secondary structure.

Surface tension studies showed that the random coil is more surface active than the helix xanthan structure. The rate of xanthan adsorption at the interface of the random coil is also faster than that of the helix structure. Surface tension was also shown to be dependent on the electrostatic potential of the polyelectrolyte. Added salt screened the electrostatic repulsive force and therefore decreased the surface tension of xanthan solution.
Effect of Molecular Conformation on the Surface Properties of Polyelectrolyte Solutions: Xanthan Gum Model Studies

by

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Finally, I dedicate this thesis to my parents and family. Without their unfailing love, encouragement and support, this thesis would not have been possible.
CONTRIBUTION OF AUTHORS

Dr. Carlos Kienzle-Sterzer defined the research project which was conducted under the guidance of Dr. J. Antonio Torres.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>LITERATURE REVIEW</td>
<td>3</td>
</tr>
<tr>
<td>Polyelectrolytes</td>
<td>3</td>
</tr>
<tr>
<td>Definition</td>
<td>3</td>
</tr>
<tr>
<td>Polyelectrolyte Solution Properties and Molecular Conformation</td>
<td>4</td>
</tr>
<tr>
<td>Parameters Affecting the Conformation of a Polyelectrolyte</td>
<td>5</td>
</tr>
<tr>
<td>Xanthan Gum</td>
<td>7</td>
</tr>
<tr>
<td>Source and Production</td>
<td>7</td>
</tr>
<tr>
<td>Structure and Conformation</td>
<td>8</td>
</tr>
<tr>
<td>Xanthan Properties</td>
<td>9</td>
</tr>
<tr>
<td>Uses of Xanthan Gum</td>
<td>11</td>
</tr>
<tr>
<td>Potentiometric Titration</td>
<td>15</td>
</tr>
<tr>
<td>Definition</td>
<td>15</td>
</tr>
<tr>
<td>Potentiometric Analysis of Polyelectrolytes</td>
<td>15</td>
</tr>
<tr>
<td>Surface and Interfacial Tension</td>
<td>18</td>
</tr>
<tr>
<td>Definition</td>
<td>18</td>
</tr>
<tr>
<td>Adsorption</td>
<td>19</td>
</tr>
<tr>
<td>Food Application</td>
<td>22</td>
</tr>
<tr>
<td>POTENTIOMETRIC TITRATION STUDIES ON XANTHAN GUM SOLUTIONS</td>
<td>27</td>
</tr>
<tr>
<td>Abstract</td>
<td>28</td>
</tr>
<tr>
<td>Introduction</td>
<td>29</td>
</tr>
<tr>
<td>Experimental Procedures</td>
<td>31</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>35</td>
</tr>
<tr>
<td>Summary</td>
<td>39</td>
</tr>
<tr>
<td>References</td>
<td>53</td>
</tr>
<tr>
<td>Table of Contents (cont.)</td>
<td>Page</td>
</tr>
<tr>
<td>---------------------------</td>
<td>------</td>
</tr>
<tr>
<td>SURFACE TENSION OF XANTHAN GUM SOLUTIONS</td>
<td>57</td>
</tr>
<tr>
<td>Abstract</td>
<td>58</td>
</tr>
<tr>
<td>Introduction</td>
<td>59</td>
</tr>
<tr>
<td>Experimental Procedures</td>
<td>60</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>62</td>
</tr>
<tr>
<td>Summary</td>
<td>68</td>
</tr>
<tr>
<td>Acknowledgment</td>
<td>69</td>
</tr>
<tr>
<td>References</td>
<td>78</td>
</tr>
<tr>
<td>LITERATURE CITED</td>
<td>81</td>
</tr>
</tbody>
</table>
**LIST OF FIGURES**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.1</td>
<td>Flow sheet diagram for the production of xanthan gum</td>
<td>25</td>
</tr>
<tr>
<td>I.2</td>
<td>Schematic representation of an adsorbed macromolecule at an interface</td>
<td>26</td>
</tr>
<tr>
<td>II.1</td>
<td>Molecular structure of xanthan</td>
<td>41</td>
</tr>
<tr>
<td>II.2</td>
<td>Potentiometric titration curves of xanthan (Cp = 8.815 x 10^{-4} equivalent/1) at different NaCl concentrations and 25°C</td>
<td>42</td>
</tr>
<tr>
<td>II.3</td>
<td>Potentiometric titration curves of xanthan (Cp = 2.204 x 10^{-3} equivalent/1) at different NaCl concentrations and 25°C</td>
<td>43</td>
</tr>
<tr>
<td>II.4</td>
<td>Potentiometric titration curves of xanthan (Cp = 4.408 x 10^{-3} equivalent/1) at different NaCl concentrations and 25°C</td>
<td>44</td>
</tr>
<tr>
<td>II.5</td>
<td>Potentiometric titration curves of xanthan (Cp = 8.815 x 10^{-3} equivalent/1) at different NaCl concentrations and 25°C</td>
<td>45</td>
</tr>
<tr>
<td>II.6</td>
<td>Plots of pk_a vs. Cs^{1/3} (NaCl concentration) of different xanthan concentration solutions at α = 0.75 and 25°C</td>
<td>46</td>
</tr>
<tr>
<td>II.7</td>
<td>Potentiometric titration curves of different xanthan concentration solutions at 25°C</td>
<td>47</td>
</tr>
<tr>
<td>II.8</td>
<td>Plots of pk_a vs. Cp (xanthan concentration) at different NaCl concentrations and 25°C</td>
<td>48</td>
</tr>
<tr>
<td>II.9</td>
<td>Potentiometric titration curves of a 8.815 x 10^{-4} equivalent/1 xanthan solution at various temperatures</td>
<td>49</td>
</tr>
<tr>
<td>II.10</td>
<td>Potentiometric titration curves of a 8.815 x 10^{-4} equivalent/1 xanthan solution at various temperatures with or without added 0.05 N NaCl</td>
<td>50</td>
</tr>
<tr>
<td>List of Figures (cont.)</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>------------------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>II.11 Theoretical and experimental plots of Δp&lt;sub&gt;k&lt;/sub&gt; vs. α of a 8.815 x 10&lt;sup&gt;-4&lt;/sup&gt; equivalent/l xanthan solution at 25°C</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>II.12 Theoretical and experimental plots of Δp&lt;sub&gt;k&lt;/sub&gt; vs. α of a 8.815 x 10&lt;sup&gt;-4&lt;/sup&gt; equivalent/l xanthan solution at 0.05 N NaCl and 25°C</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>III.1 Schematic representation of the drop weight apparatus</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td>III.2 Time dependency of surface tension measurements of different xanthan concentration solutions (α = 0.95)</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>III.3 Time dependency of surface tension measurements of different xanthan concentration solutions (α = 0.95) in 0.1 N NaCl</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>III.4 Time dependency of surface tension measurements of different xanthan concentration solutions (α = 0.6) in 0.1 N NaCl</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>III.5 Plots of equilibrium surface tension vs. log Cp (xanthan concentration)</td>
<td>77</td>
<td></td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.1</td>
<td>Surface tension of typical surfactants.</td>
<td>24</td>
</tr>
<tr>
<td>II.1</td>
<td>Electrostatic potential and $\Delta G_{el}$ of xanthan ($C_p = 8.815 \times 10^{-4}$ equivalent/l) at different salt concentrations and $25^\circ C$</td>
<td>40</td>
</tr>
<tr>
<td>III.1</td>
<td>Initial dynamic surface tension, $\gamma_0$, of different xanthan concentration solutions at different NaCl concentrations and $25^\circ C$.</td>
<td>70</td>
</tr>
<tr>
<td>III.2</td>
<td>Initial dynamic surface tension, $\gamma_0$, of xanthan solutions at different degree of dissociation ($\alpha$) and $25^\circ C$.</td>
<td>71</td>
</tr>
<tr>
<td>III.3</td>
<td>Initial dynamic surface tension, $\gamma_0^{1/4}$ of a xanthan solution ($C_p = 8.815 \times 10^{-4}$ equivalent/l) at different salt concentrations and various temperatures.</td>
<td>72</td>
</tr>
</tbody>
</table>
EFFECT OF MOLECULAR CONFORMATION ON THE SURFACE PROPERTIES OF POLYELECTROLYTE SOLUTIONS: XANTHAN GUM MODEL STUDIES

INTRODUCTION

Although the surface properties of pure liquids and dilute solutions of simple electrolytes have been repeatedly investigated, the surface properties of polymer solutions have not been extensively studied. Some workers have showed that high molecular weight compounds, e.g. proteins and polyacrylic acid, may have surface active properties (Shirokova et al., 1981; Ishiomuro et al., 1980; Keshavarz, et al., 1979). The equilibrium as well as the dynamic surface tension of polymer solutions have been suggested to play a critical role in several industrial applications including spray-drying of various solutions, emulsion stability and film formation. Most of the surface tension studies on polymer solutions have been on specific applications and have not evaluated the important relationship between the polymer conformation and the surface tension of the solution.

Xanthan is a high molecular weight polysaccharide of widespread use as a viscosity-increasing additive. Several studies have provided information on its chemical structure and physical properties (Jansson et al., 1975; Jeanes et al., 1961).
Information on the molecular conformation of this molecule has also been published (Southwick et al., 1983, 1982; Okuyama et al., 1979; Milas and Rinaudo 1979; Holzwarth, 1976; Morris et al., 1976). The information availability and widespread use were the factors considered when selecting xanthan for our model studies.

To establish basic principles for the control of the molecular structure-surface properties relationship, the specific objectives of this research project were:

1. To examine the effect of the order-disorder transition of xanthan in solution on the liquid-gas interface formation process.

2. To evaluate the effects of salts and temperature on the surface tension of xanthan solutions.
LITERATURE REVIEW

Polyelectrolytes

Definition

Polyelectrolytes are polymers containing ionogenic groups, i.e. groups that dissociate into ions when present in a solution. They combine macromolecular behavior with electrolyte properties in a non-additive way. According to the nature of the ionogenic groups they can be divided into three categories (Vogutsky, 1978).

1. Polyelectrolytes containing acid groups, e.g. -COO\(^-\) or OSO\(_3\)\(^-\). Acidic polysaccharides such as pectic acid, gum arabic, alginate, xanthan and carrageenans belong to this group.

2. Polyelectrolytes containing basic groups, e.g. -NH\(_3\)\(^+\). Basic polyelectrolytes have not been found in nature, but several have been synthesized.

3. Polyelectrolytes containing both acid and basic groups (polyampholytes). They include proteins which have -COO\(^-\) and -NH\(_3\)\(^+\) groups.

Most of the biologically important macromolecules are polyelectrolytes: proteins, nucleic acid and acidic polysaccharides. Therefore, an understanding of their structural, chemical and physical properties is particularly critical.
Polyelectrolyte Solution Properties and Molecular Conformation

The conformation of polyelectrolytes depends strongly on their primary structure. For example, most proteins have a globular conformation while DNA has a double-stranded helix structure.

The physical properties of polyelectrolyte solutions, such as viscosity and osmotic pressure, depend on the conformation of the dissolved macromolecule. The intrinsic viscosity, \([\eta]\), of a macromolecule can be defined as (van Holde, 1985b):

\[
[\eta] = Vv + ku^2C + \ldots
\]  

(1)

where \(V\) is a shape factor, \(v\) the specific volume and \(C\) the concentration of the macromolecule. The value of \(V\) for spherical particles is 2.5; any deviation from sphericity leads to larger \(V\) values and therefore to higher intrinsic viscosity. Experimental studies have shown that highly asymmetrical molecules show a higher intrinsic viscosity than spherical molecules of the same molecular weight (Smith et al., 1983).

The osmotic pressure of polyelectrolyte solutions can be defined as (Morawetz, 1965):

\[
\pi/C_2 = RT (1/M_2 + BC_2 + \ldots)
\]  

(2)

where \(\pi\) is the osmotic pressure; \(C_2\) and \(M_2\) are the concentration and molecular weight of the macromolecule; and, \(B\) is the second virial coefficient which is proportional to the excluded volume of the macromolecule. Therefore, the osmotic pressure of a polyelectrolyte solution should decrease at higher salt concentrations as a
result of a contraction of the charged chain. This shows again that molecular conformation affects the solution properties of a polyelectrolyte.

Parameters affecting the conformation of a polyelectrolyte

The conformation of a macromolecule may be stabilized by hydrogen, hydrophobic and electrostatic bonds and by Van der Waals attraction forces. Factors disrupting these interactions will affect the conformation of the macromolecule. For instance, pH will change the number of charged groups on a polyelectrolyte and therefore affect electrostatic repulsive forces. Increasing the number of charged groups could overcome intramolecular and intermolecular stabilizing forces and result in molecular conformation changes (Nagasawa and Holtzer, 1964).

The shape of macromolecules in solution is affected not only by pH changes but also by the introduction of an indifferent electrolyte. When the concentration of an electrolyte in a polyelectrolytic solution is not too high, the ionization of ionogenic groups is suppressed and the molecular conformation is stabilized. When the concentration of electrolytes are high, their salting out effect reduces the solubility of polymers and causes the formation of compact molecular coils (Smith et al., 1983).

Polymer concentration is also a factor affecting molecular shape. The chain of flexible polyions will expand in diluted solutions and the fixed charges may be separated from each other to some extent. The separation of the fixed charges will reach a limit
when the concentration increases and result in a molecular chain with rubber-like elasticity (Morawetz, 1965).

The ordered structure of macromolecules are easily destroyed by elevated temperature. Temperature increases the solution entropy and disrupts the intramolecular and intermolecular bonds that stabilize the conformation of a molecule (van Holde, 1985b).

The effects of solvents on the molecular conformation are also well known. The ratio of hydrophilic to hydrophobic groups play a very important role in solute-solvent interactions. For example, proteins are denaturated when dissolved in guanidine · HCl or urea (Smith et al., 1983).
Xanthan Gum

Sources and Production

Several microorganisms produce extracellular polysaccharides or slime capsules. These polysaccharides are bound to the cell wall by noncovalent linkages, can be easily recovered in large quantities from fermentation broths and have a large number of industrial applications.

During the mid-1950's, the Northern Utilization Research and Development Division of the USDA conducted an extensive examination of its large microbial culture collection and identified several useful biopolymers. Polysaccharide B-1459 (xanthan) produced by Xanthomonas campestris, was found to have the most significant commercial potential (Jeanes et al., 1961). Several companies carried out their pilot plant studies and a non-food-grade xanthan was produced in 1961. Substantial commercial production began in 1964. Following extensive animal trials, the Food and Drug Administration authorized in 1969 the use of xanthan in foods.

Fig. 1.1 shows a flow sheet diagram for xanthan production by aerobic fermentation. 1-5% glucose concentration have been found to produce the highest yield (Lilly et al., 1958). The production of metabolic acids and xanthan decreases the pH of the medium. If the pH falls below 5.0 xanthan production either decreases dramatically or ceases entirely. Therefore, it is necessary to add caustic soda to maintain neutral pH.
After fermentation, the broth is pasteurized at near-boiling temperature. A number of methods have been proposed for xanthan recovery from the fermentation broth. Food-grade xanthan gum is recovered by isopropyl alcohol addition. This is followed by drying, milling, testing and packaging.

Structure and Conformation

The primary structure of xanthan is shown in Fig. II.1 (Jansson et al., 1975). The backbone of xanthan consists of a cellulose-like poly β-(1-4)-D-glucan. At the 3-position of alternate glucose monomer units there is a branch consisting of a trisaccharide side chain containing one glucuronic acid and two mannose residues. The terminal β-D-mannose unit is glycosidically linked to the 4-position of β-D-glucuronic acid, which is glycosidically linked to the 2-position of α-D-mannose. The 6-position of the non-terminal D-mannose is acetylated. The degree of pyruvate substitution of the 4- and 6-position of the terminal mannose varies from 0.31 to 0.56, depending on the bacterial strain, history and fermentation condition (Sanford et al., 1977; Cadmus et al., 1976).

The secondary and tertiary structure of xanthan have been investigated considerably. X-ray diffraction studies (Okuyama et al., 1979) and electron microscopic studies (Holzwarth et al., 1977) of oriented fibers suggest that xanthan is a double-stranded helix. Sato et al. (1984) suggested that xanthan in 0.1 M aqueous NaCl has a $5_1$ double-stranded helical structure. On the other hand, spectroscopic studies (Morris et al., 1977;
Milas and Rinaudo, 1979; Norton et al., 1980) have suggested a single-stranded helix for the ordered conformation. Further studies are needed to resolve this controversy. Spectroscopic studies have also suggested that xanthan exists in solution in either a rodlike, ordered conformation or as a wormlike chain with a low degree of flexibility.

Holzwarth (1978) reported that the molecular weight of xanthan varies from $0.4 \times 10^6$ to $15 \times 10^6$. This wide range may result from an association phenomenon between polymer chains. An analysis of the complex conformation relationship between xanthan molecules should help in the interpretation of the distinctive properties of xanthan.

Xanthan Properties

1. Rheological properties

Xanthan can be dissolved in either hot or cold water to produce a high viscosity solution even at low xanthan concentration (Jeanes et al., 1961). The viscosity decreases rapidly when the rate of shear is increased. The relationship of viscosity and shear rate is instantaneous and reversible. This highly pseudoplastic behavior is important in many xanthan applications.

Another distinctive property of xanthan is its high rheological yield value. The working yield value can be defined as the shear stress required to produce a shear rate of 0.01/second (Kang et al., 1979).
2. Effect of salt

Jeanes et al. (1961) showed that the effect of salt on viscosity depends on the concentration of the xanthan solution. At xanthan concentrations of 0.1% or lower, the addition of potassium chloride reduces viscosity only slightly. The opposite effect is observed at higher xanthan concentrations. It has also been observed that the higher the gum concentration, the higher the salt concentration required to achieve maximum viscosity. Divalent salts, such as magnesium and calcium, have similar effects on viscosity. The presence of salt also improves the viscosity and conformation thermal stability of xanthan (Jeanes et al., 1961; Holzwarth, 1976; Milas and Rinaudo, 1979).

The compatibility of various polyvalent metal salts with xanthan at various pH values was shown by Pettitt (1979). Compared with trivalent ions, divalent ions are less effective in inducing xanthan gelation. High concentration of monovalent ions, however, inhibit xanthan gelation.

3. Effect of temperature

Unlike most polysaccharide solutions whose viscosity generally decrease when heated, the viscosity of xanthan solution increase after an initial decrease (Jeanes et al., 1961). Most probably, the effective hydrodynamic volume increases when the xanthan molecule changes from an ordered to a random coil conformation.

4. Effect of pH

The viscosity of xanthan solutions does not change in the 9 to 6 pH range. Between pH 5 and 4 the viscosity increase progressively.
Below pH 4 there is a linear decrease in viscosity (Jeanes et al., 1961). However, in the presence of small salt amounts, the viscosity of xanthan solutions is insensitive to pH over the range 1.5 to 13 (Kang et al., 1979).

5. Interaction with galactomannans

Xanthan gum has the ability to react with galactomannans, such as guar gum and locust bean gum (Tako et al., 1985, 1984). This interaction probably involves the side chain of the former and the backbone of the latter. In the case of guar gum a synergistic increase in viscosity has been observed (Tako et al., 1985).

Uses of Xanthan Gum

1. Industrial applications
   a. Petroleum industry

   Because of its high viscosity, shear-thinning, thermal stability, and salt compatibility, xanthan can be used as an oil well drilling fluid (Carico, 1976) and as a workover and completion fluid (Abdo, 1983). It can also be used to enhance oil recovery (Sandvik et al., 1977; Ukigai et al., 1984).

   b. Cleaners

   The good viscosity stability in high acid and alkaline conditions allow xanthan to be formulated with acid or alkaline cleaners. The strong pseudoplastic character of xanthan solutions provide enough contact time to allow adsorption to the surface being cleaned (Edwards et al., 1984).
c. Textile printing and dyeing

Xanthan is used as a thickener to prevent dye migration and therefore produces sharp and clean patterns (Grollier, 1985).

d. Other applications

Xanthan has also been used in ink (Murphy, 1984), paper and board manufacture (O'Callaghan, 1984) and ceramic glazes (McNeely et al., 1966).

2. Food Applications

Because of its unique properties xanthan has been used extensively by the food industry. These properties can be summarized as follows: (1) high viscosity at low concentration; (2) pseudo-plasticity which enhance the sensory properties of foods, e.g. mouth feel and flavor release (Kokini, 1985); (3) high working yield value which stabilizes emulsions and suspensions against separation; (4) solubility in hot or cold water; (5) little variation in viscosity with changing temperature; (6) good compatibility with a wide range of salts; (7) good emulsifying properties; and (8) freeze and thaw stability.

a. Oil-water emulsion stabilization

In oil-water emulsions (up to 60% oil), xanthan is essential to prevent creaming (Hennock et al., 1984). An emulsion may be interpreted as a suspension system where the dispersed oil globules are suspended in a thickened aqueous medium. When xanthan is present in this medium its high yield value helps to stabilize the suspension of dispersed oil globules.
b. Beverages

Citrus fruit beverages containing pulp, are stabilized by the incorporation of a mixture of xanthan and a substituted sodium carboxymethyl cellulose (Jackman, 1979). Xanthan also gives citrus and fruit-flavored beverages enhanced mouth feel with full-bodied taste and good flavor release (Schupper, 1968).

c. Frozen foods

Xanthan and locust bean gum mixture have been shown to enhance the freeze-thaw stability of frozen foods containing fat (Cheng, 1979). The freeze-thaw stability of spoonable starch-based salad dressings can also be maintained by the addition of 0.1% xanthan (Wintersdorff, 1972).

d. Bakery products

In baking applications, the addition of xanthan enhances water-binding and improves the shelf-life of cakes and breads. It can also partially replace egg in sponge mixes.

The addition of xanthan to the undenaturated wheat gluten improves bread volume and softens the crumbs (Anonymous, 1979). Xanthan is used in angel food cakes to replace certain ingredients and to increase foam stability (Miller et al., 1983).

e. Canning

Because of its unusual heat stability, xanthan has been used in heat-processed food systems containing sauces and gravies, e.g. spaghetti, cheese and barbecue sauces.
f. Process and cream cheese

A combination of xanthan, locust and guar gum has been used to prepare process cheese spreads with adequate consistency, good sliceability at refrigerated and ambient temperatures, and proper melt-down characteristics when sliced and heated (Kovacs et al., 1976).

3. Agricultural Applications
a. Animal feed

During storage or shipping the ingredients of liquid animal feed supplements always tend to stratify, settle out or alter their physical stability. Andrew (1977) found that the addition of 1 to 2 lb xanthan per ton of supplement reduces any separation or stratification of these mixtures.

b. Agricultural chemicals

Schuppner (1972) found that xanthan improves the flow of fungicides, herbicides and insecticides by uniformly suspending the solid compounds in an aqueous system. Xanthan improves also sprayability, reduces drift and increases contact time with plants.

4. Pharmaceutical and Cosmetic Applications
a. Pharmaceutical applications

Xanthan stabilizes pharmaceutical emulsion formulations (Felty, 1975) and therefore guarantees a uniform dosage.

b. Cosmetic applications

Cosmetic emulsions containing a fatty acid salt, a monoionic surfactant, bentonite and xanthan are stable and with uniform consistency (Anonymous, 1984).
Potentiometric Titration

Definition

Potentiometry is the measurement of a cell potential ($E_{\text{cell}}$). The Nernst equation can be used to relate $E_{\text{cell}}$ with activity values ($a_x$):

$$E_{\text{cell}} = (\text{constant}) \pm (\text{slope}) \log a_x$$  \hspace{1cm} (3)

Potentiometric titration is therefore the measurement of a cell potential during titration with acids or bases to obtain the activity of an electrolyte or a polyelectrolyte. Potentiometric titration is a well established and widely used analytical technique, e.g. for the determination of ionization constants in aqueous solutions, the determination of stability constants of metal ion-ligand complexes, etc.

Potentiometric analysis of polyelectrolytes

Potentiometric titration can not only be used to determine the ionization constant of a polyelectrolyte, but also to study its conformation changes. This method was first employed by Nagasawa and Holtzer (1964) to study the polyglutamic acid helix-coil transition. They found that the titration curve of polyglutamic acid is not linear as is usually the case of polyelectrolytes with a random coil structure, e.g. polyacrylic acid. Katchalsky et al. (1967) used the titration method and the optical rotation dispersion technique to study the conformation transition of pepsinogen. They found that the transition occurred in the range of ionization for the three
histidines present in pepsinogen. Titration studies by Homma et al. (1974) have suggested that the conformational transition of poly (α-DL-l-glutamic acid) occurs in the pH 3 to 5 range. Peggion et al. (1976) showed that the nonionized poly (p-amino-L-phenylalanine) can assume two ordered conformations depending on the temperature. A right-handed helical form is present at room temperature, whereas a β-structure is found at temperatures higher than 40°C. Chidambaram et al. (1985) investigated the conformational transition of poly (methacrylic acid) in 1,4-dioxane/water mixtures and found a solvent induced conformational transition.

Nagasawa et al. (1965) examined stereoregular polymethacrylic acid and suggested that the potentiometric titration curve might depend on the local conformation of the polyion skeleton rather than on the overall shape of the polyion coil. They showed that isotactic polymethacrylic acid may have a helical conformation because of the strong electrostatic repulsive between fixed polyelectrolyte, whereas atactic and syndiotactic polymethacrylic acid may have a zig-zag conformation.

Titration data can not only be used in qualitative studies of macromolecular conformation but also for the quantification of the enthalpy and entropy changes during helix-coil transitions. The value of these energy changes can be used to quantitatively analyze the stability of the helix structure of polyelectrolytes. Olander et al. (1968) studied the stability of the polyglutamic acid α helix, and found that the free energy change of the helix-coil transition depends on temperature, but only slightly on salt
concentration. Grourke et al. (1971) compared the stability of poly-L-lysine, poly-L-ornithine and poly (L-diaminobutyric acid). Their titration studies showed that the helix stability of these polypeptides is a direct function of the number of methylene groups on the side chains.

Theoretical potentiometric titration studies have also been published (Nagasawa, 1971; Katchalsky et al., 1954; Harris et al., 1954). The ionization constant of polyelectrolytes can be quantitatively obtained by calculating the electrostatic potential at the site of a dissociable charged point by the use of the Debye-Hückel linear theory or the Poisson-Boltzmann equation. Another theoretical approach has been suggested by Manning and Holtzer (1973) and it allows the calculation of the radius of molecules by modeling them as a cylindrical rod.
Surface and Interfacial Tension

Definition

The terms surface and interfacial tension are used to describe surface properties, particularly of solutions. In the bulk phase the intermolecular forces acting on any individual molecule are, on the average, equal in all directions. However, at any interface the molecules are exposed to an asymmetrical force field. Forces pulling a molecule, located at an interface between two immiscible phases, into the interior of one phase are not balanced by those pulling it into the interior of the other phase. Therefore, a surface or interfacial tension can be measured at interfaces. When both phases are condensed the term interfacial tension is used. When one bulk phase is gas or vapor the term surface tension is used instead.

At constant temperature and pressure, the relationship between the Gibbs energy change, associated with an increase in the area of an interface, and the surface or interfacial tension ($\gamma$) is given as (Hiemenz, 1977):

$$dG = rldx = rdA$$

(4)

where $ldx$ and $dA$ is the change of the interface area. Therefore, surface (interfacial) tension is treated either as a force per unit area or an energy per unit area, i.e. in the S.I. system of units (Newton) (m$^{-1}$) or (Joule) (m$^{-2}$).
Adsorption

The surface activity of a solute molecule arises primarily from the ability of the adsorbed solute molecule to alter the attractive interactions at the interface between two dissimilar molecules (air-water or oil-water) (Rosen, 1978).

Fig. 1.2 shows a polymer chain adsorbed at a solid/liquid interface. The adsorbed polymer molecule has a large number of its segments in direct contact with the surface (trains). Other parts of the molecule protrude into the solvent, as three-dimensional loops and tails (Binford et al., 1959).

Unlike small molecules, the adsorption of macromolecules takes a long time to reach equilibrium (Silberberg, 1962). The establishment of equilibrium at the newly formed surface may involve, first, diffusion of the solute to the interface; second, desolvation of adsorbed molecules; and third, molecular rearrangement in the interfacial region (Fainerman et al., 1969). To examine the kinetic of the adsorption process, Graham and Phillips (1979a) studied how the surface concentration, \( \Gamma \), and surface pressure, \( \pi \), changed during adsorption. They found that the change of surface concentration \( d\Gamma/dt \) can be explained in terms of the following steps:

1. \( \pi \) and \( \Gamma \) changing -- rate is diffusion controlled.
2. (a) \( \pi \) and \( \Gamma \) changing -- positive energy barrier to penetration and molecular rearrangement at the interface.
   (b) \( \pi \) changing and \( \Gamma \) constant -- conformation changes occur in the adsorbed layer.
The molecular conformation will be partially denaturated during adsorption at the interface. Graham and Phillips (1979b) described the adsorption of β-casein in terms of segments of the disordered polypeptide chain forming trains of amino acid residue at the interface with loops and tails of residues protruding into the bulk phases. At higher β-casein concentrations, more and more protein molecules are available and further adsorption may occur with formation of multilayers. Since multilayers arise only through polymer-polymer interactions no change in native ordered structure will occur.

The thermodynamic treatment solute adsorption at interfaces as developed by Gibbs lead to the following expression:

\[
\Gamma = \frac{-1}{2.303 RT} \frac{d\gamma}{d\log C}
\] (5)

Eq. (5) suggests that the surface excess of the solute, \( \Gamma \), can be obtained from the slope of a plot of \( \gamma \) (surface tension) versus the logarithm of the solute concentration.

Statistical mechanics procedures and computer simulations have been recently reviewed by Vincent and Whittington (1982). The objectives of these theories are to predict the main properties of the system, including the fraction in the form of trains, the thickness of the interfacial region, \( \delta \), and the distribution of the polymer residues in the interfacial region, in terms of the solvent properties, the nature and the interaction of the polymer with the solvent, the length of the polymer chain and the extent of the adsorption.
Surface adsorption has been found to be molecular weight dependent. For instance, Sarkar (1984) found that the interfacial tension of hydroxypropyl methylcellulose in a water/octane system increased with molecular weight. High molecular weight polymers may have a tendency to form at the interface loops extending into the bulk phase. Therefore, the relative density of surface active groups at the interface would be low.

The structure of macromolecules also affect their surface adsorption. Adams et al. (1971) found that heat-denaturated acetyl lysozyme unfolds at the interface more than unheated lysozyme. Analyzing adsorption data for β-casein, bovine serum and lysozyme, Graham and Phillips (1979b) also found that flexible and less ordered proteins were more surface active than globular proteins.

pH and ionic strength effects on surface tension have also been reported. Sato et al. (1979) found that surface tension of gelatin increases in the acidic region below pH 4.5 and in the basic region above pH 8 because of increasing repulsive forces between positive or negative charges. The pH dependence of surface tension is also found in polyacrylic acid and polymethacrylic acid (Ishimuro et al., 1980a; Katchalsky et al., 1951). Surface properties are also affected by ionic strength. Studies on polyacrylic acid in sodium chloride solutions have found a linear relationship between equilibrium surface tension and the logarithm of salt concentration. Salt screens the repulsive forces between the adsorbing and other
adsorbed molecule facilitating the adsorption. The same effect has been observed in sodium alkyl sulfate solutions (Fainerman et al., 1982).

Food Applications

Food processing operations involving foams and emulsions depend strongly on interfacial properties. Milk, cream, butter, ice cream, margarine, salad dressings and mayonnaise are typical food examples where foaming and emulsion are critical product parameters. Furthermore, the formation of emulsions may be an important intermediate state in food processing, as in the case of many semi-moist foods, powdered toppings, cake mixes, etc.

Two steps are involved in the preparation of foams and emulsions. First, interfacial tension is lowered to help create new interfacial surface by the addition of surface active agents at the concentrations indicated in Table I.1.

When lowering interfacial tension, smaller surfactants can be more effective than macromolecules. Smaller molecule may also have a more significant role in reducing re-coalescence (Stainsby, 1985). The second stage is the stabilization of the foam or emulsion already formed. There are three different stabilization mechanisms to consider: charge stabilization, steric stabilization, and stabilization by adsorbed solute at the interface. This long term stability is due almost entirely to the macromolecular adsorption and rearrangement at the interface (Tadro and Vincent, 1983).

Polysaccharides and proteins are used in foams and emulsions. Although polysaccharides are generally thought to be hydrophilic even when they contain hydrophobic -CH groups. The glycosidic bonds
between monomers are much less flexible and can not fold as tightly as polypeptides. In addition, they are more homogeneous than proteins. In contrast, a wide variety of side chains are present in proteins, ranging from hydrocarbons and aromatics to polar and ionizable forms. Moreover, some of the more important food proteins form in aqueous solution highly flexible and disordered structures (Whitney, 1977). For all these reasons and compared to polysaccharides, proteins play a more important role at interfaces. Nevertheless, many polysaccharides (e.g. xanthan amylose, methylcellulose, pectins) are surface active agents (Prud'homme and Long, 1983). However, they are not as effective as proteins in water/oil systems because polysaccharides are unable to form loops and tails in an oil phase. These observations would probably explain why their surface properties have not been extensively studied.
Table I.1. Surface tension of typical surfactants.

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>Concentration</th>
<th>Surface Tension</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>sorbitan monostearate</td>
<td>1%</td>
<td>46</td>
<td>food</td>
</tr>
<tr>
<td>polyoxyethylene sorbitan monostearate</td>
<td>1%</td>
<td>43</td>
<td>food, pharmaceuticals</td>
</tr>
<tr>
<td>polyoxyethylene sorbitan tristearate</td>
<td>1%</td>
<td>31</td>
<td>food</td>
</tr>
<tr>
<td>polyoxyethylene sorbitan monooleate</td>
<td>1%</td>
<td>41</td>
<td>food, pharmaceuticals</td>
</tr>
<tr>
<td>polyoxyethylene alkylphenols (Igepal Co-630)</td>
<td>0.01%</td>
<td>30</td>
<td>textile, detergent</td>
</tr>
<tr>
<td>polyoxyethylene ester of fatty acid (Sterox CD)</td>
<td>1%</td>
<td>40</td>
<td>detergent</td>
</tr>
<tr>
<td>polyoxyethylene mercaptans (Nonic 218)</td>
<td>0.01%</td>
<td>38.1</td>
<td>shampoos</td>
</tr>
<tr>
<td>polyoxyethylene fatty alkylamines (Ethomeen C/15)</td>
<td>1%</td>
<td>33</td>
<td>petroleum</td>
</tr>
<tr>
<td>phosphate ester of nonylphenol, 6E0</td>
<td>1%</td>
<td>32</td>
<td>plating bath, laundering formulation</td>
</tr>
<tr>
<td>octadecylsulfuric acid</td>
<td>1%</td>
<td>41.6</td>
<td>shampoos</td>
</tr>
<tr>
<td>sodium decyl a-sulfobutyrate</td>
<td>0.2%</td>
<td>36.9</td>
<td>detergent</td>
</tr>
<tr>
<td>lauryle sodium phosphate</td>
<td>0.25%</td>
<td>36</td>
<td>detergent, suspending agent</td>
</tr>
</tbody>
</table>
Figure I.1  Flow sheet diagram for the production of xanthan gum

Xanthomonas campestris culture → Inoculum build-up → Seed tank → Fermenter → Pasteurizer → Gum recovery by solvent

Packing → Mill → Dryer
Figure I.2  Schematic representation of an adsorbed macromolecule at an interface
POTENTIOMETRIC TITRATION STUDIES ON

XANTHAN GUM SOLUTIONS

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Abstract

The potentiometric behavior of xanthan solutions were studied as a function of ionic strength, polymer concentration and temperature. For a given value for the polymer dissociation constant, $\alpha$, $p_{k_{a}}$ and $C_{s}^{1/3}$ (salt concentration) values followed a linear relationship. At polymer concentrations below $6.5 \times 10^{-3}$ (equivalent/l), $p_{k_{a}}$ was a function of polymer concentration. However, when the polymer concentration was higher than $6.5 \times 10^{-3}$ (equivalent/l), $p_{k_{a}}$ was independent of polymer concentration. At high salt concentrations, polymer concentration changes affected only slightly the potentiometric behavior of xanthan solutions. Temperature increases disrupted the xanthan helix ordered conformation; this effect was reduced by added salt confirming the work by Rinaudo et al. (1981). Titration data and Manning's limiting law were used to estimate the radius of the xanthan cylindrical rod at 2.2 nm.
Introduction

The specific structure and conformation of xanthan is responsible for its unusual solution properties and wide commercial applications. This extracellular polysaccharide is produced by the bacterium *Xanthamonas campestris* and consists of a poly [(1→4)-β-D-glucan] chain with a β(1→3) substituted trisaccharide side chain (Fig. 2.1). About 25 to 50% of the side chains contain pyruvate substitutes. The degree of substitution has been shown to be an important parameter, strongly affecting the physical properties of xanthan solutions (Sanford *et al.*, 1977).

The secondary and tertiary structure of xanthan has been studied for years but no definite conclusion has yet been reached. Electron microscopy studies by Holzwarth *et al.* (1977) suggest that the ordered conformation of this polymer is a double-stranded helix. This proposed structure was confirmed by Sato *et al.* (1984a). However, a single stranded helix was proposed by Morris *et al.* (1977) and supported by the work of Milas and Rinaudo (1979) and Norton *et al.* (1980).

Spectroscopic experiments such as optical rotatory dispersion, circular dichroism, NMR and light scattering (Southwick, *et al.*, 1981; Milas and Rinaudo, 1979; Morris *et al.*, 1977; Holzwarth, 1976) have confirmed the existence in aqueous salt solutions of a xanthan ordered conformation that undergoes a thermal order-disorder transition.

Potentiometric titration methods have been extensively studied, both from theoretical and experimental points of view, to understand the behavior of polyelectrolytes. However, complete potentiometric
Titration studies on the effects of temperature, ionic strength and polymer concentration on xanthan conformation have not yet been published. This paper employed this method to study these effects and to establish the role of carboxylate charged groups in polyelectrolyte conformation.
Experimental Procedures

Material

A commercial sample of xanthan gum was obtained from Sigma Co. (No. G-1253). A weight average molecular weight of about 2 x 10^6 was determined by intrinsic viscosity measurements (Sato et al., 1984b). The sodium ion content of the commercial sample was 1.1 x 10^-3 equivalent/g, measured with an Orion combination sodium electrode (model 96-11) connected to an Orion microprocessor pH/millivolt meter (model 811). The chloride ion content was 0.26 x 10^-3 equivalent/g, measured with an Orion halide electrode (model 94-17B) with a double junction reference electrode (model 90-02).

Fresh xanthan solutions were prepared with distilled water just before performing each titration experiment. The polymer concentration range studied was 8.815 x 10^-4 to 8.815 x 10^-3 equivalent/l. Salt was added in the range of 0.05 N to 1 N. Temperature was controlled between 25° and 70°C. The initial pH varied from 5.3 to 6.2 depending upon xanthan concentration, salt concentration and temperature.

Methods

For xanthan concentrations under 4.408 x 10^-3 equivalent/l, 50 ml commercial xanthan solutions were titrated with 0.1N HCl in a 100 ml vessel. To control the solution temperature the vessel had a water jacket connected to a Brickman Lauda refrigerating circulator (model RMT-6, accuracy ± 0.1%). Titration was made with a Metromh 655 Multi-Dosimat with a 5 ml exchange unit (accuracy ± 0.005 ml). The pH values were read to 0.001 pH units using an Orion pH electrode.
(model 91-02). 1 N HCL was used for xanthan concentrations above 4.408 x 10^{-3} equivalent/l. In this concentration range a gel-like structure was formed and the pH values were read using an Orion combination-flat pH electrode (model 91-35).

Analysis of Titration Data

The degree of ionization, \( \alpha \), can be calculated from the following chemical reactions of the components present in the xanthan solutions: \( \text{H}_2\text{O}, \text{HCl}, \text{NaCl}, \) and the commercial xanthan sample, i.e. \( \text{"RCOO}^-\text{Na}^+" \).

\[
\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-
\]
\[
\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-
\]
\[
\text{RCOO}^-\text{Na}^+ \rightarrow \text{RCOO}^- + \text{Na}^+
\]
\[
\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}
\]
\[
\text{RCOO}^- + \text{H}^+ = \text{RCOOH}
\]

From electroneutrality considerations we obtain:

\[
\left[\text{RCOO}^-\right] = \left[\text{Na}^+\right] + \left[\text{H}^+\right] - \left[\text{Cl}^-\right] - \left[\text{OH}^-\right] 
\tag{1}
\]

\( \alpha \) is defined as

\[
\alpha = \frac{\left[\text{RCOO}^-\right]}{\left[\text{RCOO}^-\right] + \left[\text{RCOOH}\right]} = \frac{\left[\text{RCOO}^-\right]}{\left[\text{RCOOH}\right]_{\text{total}}} 
\tag{2}
\]

where \( \left[\text{RCOOH}\right]_{\text{total}} \) is the total monomer concentration of the xanthan solution. The monomer molecular weight is \( \approx 1000 \).

From (1) and (2) we obtain:

\[
\alpha = \frac{\left[\text{Na}^+\right] + \left[\text{H}^+\right] - \left[\text{Cl}^-\right] - \left[\text{OH}^-\right]}{\left[\text{RCOOH}\right]_{\text{total}}} 
\tag{3}
\]
From the conventional dissociation constant, \( K_0 \), defined as:
\[
K_0 = [\text{RCOO}^-](H^+)/[-\text{RCOOH}]
\] (4)
we obtain:
\[
\text{pH} = \text{pk}_0 - \log[(1-\alpha)/\alpha]
\] (5)
\( \text{pk}_0 \) can be related to the standard free energy change of the ionization process, \( \Delta G^0 \).
\[
\text{pk}_0 = -\log k_0 = 0.434 \frac{\Delta G^0}{RT}
\] (6)
The apparent dissociation constant for a polyacid, \( \text{pk}_a \), is defined as follows:
\[
\text{pH} = \text{pk}_a - \log [(1-\alpha)/\alpha]
\] (7)
During the titration of a polyion, the removal of \( H^+ \) from the polyelectrolyte requires an additional work term, \( \Delta G_{el} \). Therefore, the \( \text{pk}_a \) of the polyelectrolyte solution can be expressed as (Nagasawa et al., 1965; Katchalsky et al., 1954; Harris et al., 1954):
\[
\text{pk}_a = 0.434 \left( \frac{\Delta G^0 + \Delta G_{el}}{RT} \right)
\] (8)
and
\[
\text{pH} = \text{pk}_0 - \log \left[(1-\alpha)/\alpha\right] + 0.434 \frac{\Delta G_{el}}{RT}
\] (9)
Since \( \Delta G_{el} \) can be expressed as:
\[
\Delta G_{el} = N_a e \psi_b
\] (10)
where \( N_a \) is the Avogadro number, \( e \) the charge of a proton, and \( \psi_b \) the electrostatic potential of the polyelectrolyte, eq. (9) can be modified as follows:
\[
\text{pH} = \text{pk}_0 - \log \left[(1-\alpha)/\alpha\right] + 0.434 e \frac{\psi_b}{kT}
\] (11)
where \( k \) is the Boltzmann constant and \( T \) is the absolute temperature. This allows the calculation of \( \psi_b \) and \( \Delta G_{el} \) using titration data.
Other theoretical models have been developed for the titration curve of a polyelectrolyte. The approach suggested by Manning and Holtzer (1973) allows the use of potentiometric titrations to calculate the polymer cylinder radius.

\[ p_{k_a} = p_{k_0} - g(\alpha) \log \kappa^2 a^2 \] (12)

where \( \kappa \) is the Debye-Hückel screening parameter and "a" is the polymer cylinder radius. \( g(\alpha) \) is defined as:

\[ g(\alpha) = \begin{cases} \alpha/a_1 & \text{if } \alpha < a_1 \\ 1 & \text{if } \alpha > a_1 \end{cases} \] (13)

where \( a_1 \) is the degree of dissociation of the ionizable group, measured at the critical charge density, \( E = 1 \). \( E \) is defined as:

\[ E = e^2/DkTb \] (14)

where \( D \) is the bulk dielectric constant of the solvent, and \( b \) is the average distance between charged groups. \( b \) can be defined as:

\[ b = L/V \] (15)

where \( V \) is the number of charged groups on the chain and \( L \) is the maximum end-to-end chain length.
Results and Discussion

Fig. 2.2 shows the relationship between $p_k$ and the degree of ionization $\alpha$ of xanthan gum ($C_p = 8.815 \times 10^{-4}$ equivalent/l) at different salt concentrations and $T = 25^\circ C$. All the titration curves show an ionization induced conformational transition at $\alpha \approx 0.8$. As previously mentioned, the ordered form of xanthan is a double or single helix structure. This structure is probably stabilized by hydrogen bonds between the carboxylate groups and the hydroxyl groups in the chains. This form is transformed into a random coil when the electrostatic repulsive force increases with the ionization of the carboxylate groups. The same results have been obtained in the titration of polypeptides and polymethacrylic acid (Gundiah et al., 1985; Senior et al., 1971; Nagasawa et al., 1965, 1964). Titration curves shown in Fig. II.2 suggest that the salt-form xanthan gum before titration with HCl is always in the random coil range ($\alpha$ above 0.8) which agrees with Lambert et al. (1985) who postulated that the sodium form of xanthan is a stretched coil. When the salt concentration is increased, the degree of ionization shifts to a higher $\alpha$ value for a given $p_k$. This behavior is due to the salt reduction of the electrostatic repulsive force on the xanthan charged groups favoring proton dissociation. Titration curves at higher polymer concentrations shown in Figs. II.3, II.4, and II.5, show similar effects of ionic strength.

Table II.1 shows the electrostatic potential $\psi_b$ (mv), $p_k$ and $\Delta G_{el}$ (Kcal) of xanthan at different salt concentrations. Values of $p_k$ in Fig. II.2 were extrapolated to $\alpha = 0$ (Olander
et al. 1968) to calculate values of $\Delta G_{e1}$ and $\psi_b$ using eqs. (9) and (11), respectively. Table II.1 shows that $\Delta G_{e1}$ increases when the electrostatic potential increases and the ionic strength decreases. The same effect has been shown with other materials (Kienzle-Sterzer, 1984; Ishikawa, 1979; Ohno, 1973; Nagasawa, 1971; Dubin and Strauss, 1970).

To show the effect of the ionic strength on the electrostatic nature of the solution, values of $p_{ka}$ and $C_s^{1/3}$ (salt concentration) at $\alpha = 0.75$ are represented in Fig. II.6. These values follow a linear relationship with increasing slope values as the polymer concentration increases. This indicates that the ionic strength effect becomes smaller when the polymer concentration is higher.

Fig. II.7, potentiometric titrations at various polymer concentrations in the absence of added salt and $T = 25^\circ$C, shows that the values of $p_{ka}$ increase with increasing dilution. Most probably the proton removal probability from the polymer into the external aqueous phase increases with increasing dilution, and thus increases the repulsive force. Further dissociation of the carboxylate groups would be more difficult when the net charge on the polymer increases, and hence the $p_{ka}$ values increase with increasing dilution. The same results have been shown with carboxymethyl amylose and carboxymethyl cellulose (Trivedi et al. 1981; Patel et al. 1971; Chowdhury et al. 1963; Kagawa et al. 1951).
To visualize the effect of the polymer concentration on the xanthan potentiometric behavior, plots of $p_{k_a}$ against polymer concentration ($C_p$) at different salt concentrations and $\alpha = 0.75$ were prepared (Fig. II.8). Two behaviors are observed, one for polymer concentrations above $6.5 \times 10^{-3}$ (equivalent/l) where $p_{k_a}$ is independent of the polymer concentration, and another one for polymer concentrations below $6.5 \times 10^{-3}$ (equivalent/l) where $p_{k_a}$ decreases as $C_p$ increases. Probably this is due to self-association of xanthan decreasing $p_{k_a}$ when the polymer concentration increases. When the polymer reached a certain concentration $p_{k_a}$ changed only slightly with increasing concentration. This could be due to the formation of liquid crystalline domains (Lim et al., 1984). Fig. II.8 shows also that in the presence of high salt concentrations, $p_{k_a}$ is only slightly affected by polymer concentration. Probably this is due to the difference in the electrostatic potential of the different polymer concentration which are reduced at the higher salt concentrations.

Fig. II.9 shows the effect of temperature on the potentiometric behavior of xanthan. The shape of the titration curve is irregular and the helix-coil transition point shifts to lower degree of ionization values. Probably this is due to heat disruption of the intramolecular hydrogen bonds. Therefore, even a low degree of ionization can cause an order-disorder transition. The ordered conformation can be stabilized by adding salt due to the salt screening effect on the electrostatic repulsion between the charged groups (Fig. II.10) and agrees with published results (Rinaudo and Milas, 1981, 1979; Morris et al. 1977; Holzwarth, 1976).
A rod-like molecule has been suggested for the xanthan molecule in solution. The average distance "b" between charged groups of the salt-form xanthan is 0.647 nm (Norton et al. 1984). Eqs. (14) and (15) can be used to calculate $\alpha_1$, giving a value of 0.906. Assuming a radius "a" for the cylindrically symmetric model, $p_{k_a}$ values can be theoretically calculated for different $a$ values using Manning's limiting law (Eq. 12). Fig. II.11 shows that in the absence of added salt theoretical values of $\Delta p_k$ ($\Delta p_k = p_{k_a} - p_{k_o}$) versus $a$ agree well with experimental data in the helical range ($0.53 < a < 0.8$) when $a = 2.2$ nm is chosen. This value is consistent with electron microscopy measurements ($a = 2$ nm, Holzwarth et al. 1977). However, the radius decreases dramatically to $a = 0.45$ nm in the presence of 0.05 N NaCl (Fig. II.12). This is in disagreement with published values which have shown that the hydrodynamic radius increases with ionic strength, and that the conformation is only slightly affected when the ionic strength is greater than $10^{-2}$ N (Southwick et al. 1983; Rinaudo et al. 1978). Unfortunately, Manning's limiting law has been developed for polyelectrolytes whose radius decreases with increasing ionic strength. For stiff-chain polymers, such as xanthan, this theory cannot be applied in added salt solutions.
Summary

Our potentiometric titration studies have confirmed the significance of the hydrogen bond and the carboxylate group on the secondary structure of xanthan. In particular, we have shown that the ordered xanthan conformation is stabilized mainly by hydrogen-bonds which can be disrupted by increasing the electrostatic potential of the molecule or by increasing the solution temperature. In our studies, neither the ionic strength nor the polymer concentration did affect the secondary structure of xanthan at 25°C. However, ionic strength should reduce the repulsive force between xanthan charged groups; this would explain the salt stabilization of the xanthan secondary structure at higher temperature as observed by us and other workers.

The radius of the xanthan cylindrical rod at low ionic strengths was calculated using Manning’s limited law. The values, 2.2 nm, compared well with published results. A suitable theory, however, should be developed to analyze the potentiometric data for stiff chain polymers in the presence of added salt.
Table II.1. Electrostatic potential and $\Delta G_{el}$ of xanthan
\((C_p = 8.815 \times 10^{-4} \text{ equivalent/l})\) at different
salt concentrations and 25$^\circ$C.

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
</tr>
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<tbody>
<tr>
<td>$\psi$(mv)</td>
<td>40.57</td>
<td>45.90</td>
<td>54.19</td>
<td>64.26</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NaCl (N)</th>
<th>$pK_o$</th>
<th>$\Delta G_{el}$ (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.275</td>
<td>0.935 1.057 1.248 1.480</td>
</tr>
<tr>
<td>0.05</td>
<td>2.85</td>
<td>0.648 0.791 0.989 1.467</td>
</tr>
<tr>
<td>0.10</td>
<td>2.675</td>
<td>0.614 0.750 0.955 1.344</td>
</tr>
<tr>
<td>0.25</td>
<td>2.410</td>
<td>-- 0.703 0.873 1.317</td>
</tr>
</tbody>
</table>
Figure II.1  Molecular structure of xanthan
Figure II.2  

Potentiometric titration curves of xanthan 
(Cp = 8.815 x 10^{-4} equivalent/1) at different 
NaCl concentrations and 25°C.

Concentrations of NaCl (N): □, 0.00; +, 0.05; 
♦, 0.10; Δ, 0.25; X, 0.50; ▽, 1.00.
Figure II.3 Potentiometric titration curves of xanthan (Cp = 2.204 x 10⁻³ equivalent/1) at different NaCl concentrations and 25°C

Concentrations of NaCl(N): □, 0.00; +, 0.05; ♦, 0.10; △, 0.25; ×, 0.50; ▽, 1.00.
Figure II.4 Potentiometric titration curves of xnathan ($C_p = 4.408 \times 10^{-3}$ equivalent/l) at different NaCl concentrations and $25^\circ C$.

Concentrations of NaCl (N): $\square$, 0.00; $\perp$, 0.05; $\blacklozenge$, 0.10; $\bigtriangleup$, 0.25; $\times$, 0.50; $\bigtriangledown$, 1.00.
Figure II.5 Potentiometric titration curves of xanthan (Cp = 8.815 x 10^{-3} equivalent/l) at different NaCl concentrations and 25°C

Concentrations of NaCl (N): □, 0.00; †, 0.05; ◆, 0.10; △, 0.25; ×, 0.50; ▽, 1.00.
Figure II.6  Plots of $pK_a$ vs. $\text{Cs}^{1/3}$ (NaCl concentration) of different xanthan concentration solutions at $\alpha = 0.75$ and $25^\circ\text{C}$.

Concentrations of xanthan solution (equivalent/l): 
$\Delta$, $8.815 \times 10^{-4}$; $\Box$, $2.204 \times 10^{-3}$; 
$\bigcirc$, $4.408 \times 10^{-3}$; $\blacksquare$, $8.815 \times 10^{-3}$.
Figure II.7  
Potentiometric titration curves of different xanthan concentration solutions at 25°C

Concentrations of xanthan solution (equivalent/l):
□, 8.815 x 10⁻⁴; +, 2.204 x 10⁻³;
◊, 4.408 x 10⁻³; △, 8.815 x 10⁻³.
Figure II.8  Plots of $pK_a$ vs. $C_p$ (xanthan concentration) at different NaCl concentrations and 25°C

Concentrations of NaCl(N): $\triangle$, 0.00; $\square$, 0.05; $\bigcirc$, 0.10; $\blacksquare$, 0.25; $\bullet$, 0.50; $\blacktriangle$, 1.00.
Figure II.9  Potentiometric titration curves of a $8.815 \times 10^{-4}$ equivalent/l xanthan solution at various temperatures

Temperature ($^\circ$C): $\Box$, 25; $\dag$, 35; $\blacksquare$, 50; $\Delta$, 70.
Figure II.10  

Potentiometric titration curves of a $8.815 \times 10^{-4}$ equivalent/l xanthan solution at various temperatures with or without added 0.05 N NaCl

Curve conditions:  
- $\square$, $35^\circ C$ without added salt;  
- $\triangle$, $35^\circ C$ in 0.05 N NaCl;  
- $\diamond$, $50^\circ C$ in 0.05 N NaCl;  
- $\dagger$, $70^\circ C$ in 0.05 N NaCl.
Figure II.11 Theoretical and experimental plots of $\Delta pK$ vs. $\alpha$ of a $8.815 \times 10^{-4}$ equivalent/l xanthan solution at $25^\circ C$.

Experimental curve, $\Box$; theoretical calculated curve with $\alpha = 2.2$ nm, $\times$. 
Figure II.12 Theoretical and experimental plots of $\Delta pK$ vs. $a$ of a $8.815 \times 10^{-4}$ equivalent/l xanthan solution at 0.05 N NaCl and $25^\circ C$

Experimental curve, $\square$; theoretical calculated curve with $a = 0.45 \text{nm}$, $\times$. 
References


SURFACE TENSION OF XANTHAN GUM SOLUTIONS

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Abstract

The effects of ionic strength, temperature, degree of ionization and polymer concentration on the surface tension of xanthan solutions were determined by the drop-weight and the Wilhelmy plate methods. Drop weight experiments showed that increasing ionic strength and temperature slightly decreased the initial dynamic surface tension. Increasing concentration resulted in a reverse effect. Varying the degree of ionization did not affect the initial dynamic surface tension.

Wilhelmy plate experiments showed that the surface tension of xanthan solution is time dependent. Salt addition and increased polymer concentration decrease significantly the equilibrium surface tension and the time required to reach equilibrium. The surface tension also decreased by increasing the degree of ionization of xanthan in solution. According to previous experiments (Young et al., 1986), this finding suggests that the random coil is more surface active than the helix structure and that the rate of adsorption of the random coil is also faster than that of the helix structure. Surface excess values calculated by the Gibbs equation reveal that the surface tension depends on the total proportion of segments adsorbed at the interface. The Wilhelmy plate method was also able to determine the critical concentration for liquid crystal formation.
Introduction

Xanthan, a polyelectrolyte produced by the bacterium *Xanthomonas campestris*, consists of a main chain of poly β-1,4-linked D-glucose units and of trisaccharide side chains alternately attached to the main chain (Jansson et al., 1975). This high molecular weight polysaccharide has a large number of industrial applications and several studies on its conformation and physical properties have been published (Young et al., 1986; Southwick et al., 1983, 1982; Okuyama et al., 1979; Milas and Rinaudo, 1979; Whitcomb, 1978; Holzwarth, 1976; Morris et al., 1976). Surface properties are critical in many industrial applications such as in the preparation and stability of food emulsions, enhanced oil recovery, formulation of agricultural sprays and in paper sizing. However, comprehensive studies on the surface properties of xanthan solutions have not been published.

The drop weight and the Wilhelmy plate methods can be used to examine the effects of the degree of ionization, salt, temperature and polymer concentration on the surface tension of xanthan solutions. Information on the molecular conformation of xanthan in aqueous solutions is also available (Young et al., 1986), and allows the determination of the relationship between molecular conformation and surface properties.
Experimental Procedures

Material

The weight molecular weight, sodium ion and chloride ion content of the commercial sample used in this study (Sigma Co. No. 6-1253) had been previously determined (Young et al., 1986). The values were $2 \times 10^6$, $1.1 \times 10^{-3}$ equivalent/g and $2.6 \times 10^{-4}$ equivalent/g, respectively. Fresh xanthan solutions at various degrees of ionization, $\alpha$, were prepared by HCl titration (Young et al., 1986) before each experiment.

Methods

Figure III.1 shows the apparatus used to determine the dynamic surface tension of xanthan solutions by the drop weight method. A Gilmont micrometer capillary valve (M) (Cat. No. M7100) was used to control the drop formation speed. A sample reservoir (R) was connected to the capillary valve. The temperature of the reservoir was controlled to $\pm 0.1^{\circ}C$ by a water jacket connected to a Brinkmann Lauda refrigerating circulator (Model RMT-6). A metal tip (T) was connected to the bottom of the capillary valve. A close flask (F) was used to collect drops of the solution being studied. To maintain the whole apparatus at the same temperature, cotton was wrapped around the AB glassware area. The flask was immersed in a temperature controlled water bath.

The dynamic surface tension $\gamma$, was calculated as follows (Harkins, 1919):

$$\gamma = \frac{M_d g}{2RF}$$

(1)
where $M_d$ is the drop weight, $R$ is the radius of the tip, $g$ is the gravitational acceleration constant and $F$ is a correction factor (Adamson, 1976). $M_d$ was determined in a Sartorius balance model 1615 MP6-BCD (precision = 0.1 mg). To avoid micrometer measurement error, the radius of the tip was calculated from distilled water $M_d$ values and calibration data from Jho et al. (1983).

The surface tension time dependency was determined at room temperature (approx. 22 to 25°C) by the Wilhelmy plate method (Gaines, 1966). A thin platinum plate connected to a Cahn 2000 electrobalance (accuracy ± 0.1%) was kept in a closed chamber. After determination of the initial weight, $W_0$, the plate was dipped into the xanthan solution, and the weight, $W_t$, was recorded at various time intervals.

The surface tension, $\gamma_t$, can be calculated from (Adamson, 1976):

$$ (W_0 - W_t) = 2l\gamma_t $$

(2)

where $l$ is the width of the plate (5.1 cm).

To avoid errors in the measurement of the plate immersed depth, the same geometry and solution volume were used in all experiments. This allowed the use of distilled water surface tension measurements to correct the values obtained for xanthan solutions as follows:

$$ \frac{\gamma_{\text{water measurement}}}{\gamma_{\text{xanthan measurement}}} = \frac{\gamma_{\text{water}}}{\gamma_{\text{xanthan}}} $$

(3)

where $\gamma_{\text{water}} = 72.2$ dyne/cm.
Results and Discussion

Table III.1 shows initial dynamic surface tension ($\gamma_0$) measurements, at 25°C, of solutions at different xanthan and salt concentrations. $\gamma_0$ measures the spontaneous coverage of surface at time zero and is obtained by extrapolating the surface tension to time zero. Increasing the salt concentration slightly decreases the initial dynamic surface tension because of the salt screening effect of the electrostatic charge on the polyelectrolyte. This facilitates the adsorption of the polymer on the air surface. Similar observations have been reported in polyacrylic acid solutions (Ishimuro et al., 1980). $\gamma_0$ increases with polymer concentration. The reason for this is not clear, although it is possible at higher xanthan concentrations the surface hydrophilic groups concentration will also increase and lead to lower initial surface adsorption.

The degree of ionization of xanthan had no statistically significant effect on $\gamma_0$ (Table III.2) even though potentiometric studies had shown that a conformation change occurs at $\alpha \approx 0.8$ (Young et al., 1986). This indicates that the initial dynamic surface tension of xanthan solutions is not significantly affected by polymer conformation.

As shown in Table III.3, $\gamma_0$ decreased slightly when temperature increased. The reason for this is not clear, however we should note that the surface tension of water increases when temperature is decreased (Jho et al., 1983).
The surface tension time dependency of solutions at various xanthan concentrations ($\alpha = 0.95$), was measured by the Wilhelmy plated method (Fig. III.2). As expected, surface tension decreases with time. This is consistent with the accepted interpretation of the macromolecular adsorption process: (1) diffusion of the solute to the interface; (2) desolvation of adsorbed solutes; and, (3) molecular rearrangement in the interfacial region (Ueberreiter et al., 1977, 1974; Adams et al., 1971; Fainerman et al., 1969).

Fig III.2 shows also that the equilibrium surface tension, $\gamma_\infty$, decreased when the xanthan concentration increased which is due to an increase in the interfacial xanthan concentration. The same results were obtained in humic acid and gelatin studies (Hayano et al., 1982; Sato et al., 1979). As the xanthan concentration increases, the rate and probability of molecular collision increases. Therefore, the time required to reach the equilibrium surface tension should decrease as shown in Fig. III.2.

The large surface tension drop with time suggests that xanthan could stabilize an emulsion not only by increasing the viscosity of the continuous phase but also by reducing the surface tension.

Figure III.2 also shows a sudden surface tension increase at 8.815 g/l. This suggests that at this concentration molecules aggregate to form liquid crystalline domains (Lim et al., 1984) and explains the abrupt change in surface tension values. This concentration value is slightly higher than the value ($= 6.5$ g/l) determined by potentiometric titration (Young et al., 1986).
Figure III.3 shows the surface tension time dependency of solutions at various xanthan concentrations \((\alpha = 0.95)\) and 0.1 N NaCl. A comparison with Fig. III.2, indicates that the time required to reach \(\gamma_\infty\) is shorter and that \(\gamma_\infty\) values are much lower in the presence of 0.1 NaCl than in the absence of added salt. This observation suggests that the rate and the interfacial solute concentration depend on the electrostatic potential on the polyelectrolyte. We know that when a macromolecule adsorbs at the surface, only a fraction of the molecule is directly in contact with the surface to form trains. The remainder dissolves in the solvent, as loops and tails (Vincent et al., 1982). When segments of a molecule move to the surface, intermolecular and intramolecular interactions occur between the adsorbing molecule and the molecules already adsorbed. The loops and tails of polyelectrolytes contain charged groups and constitute an electrical barrier to the surface adsorption process. The addition of salt decreases the electrostatic repulsive force of these charged groups, increasing the rate of adsorption and the amount of adsorbing segments at the interface. Again identical results were found in studies on marine humic acid and polyacrylic acid (Hayano et al., 1982; Ishimuro et al., 1980).

Figure III.4 shows surface tension measurements at different xanthan concentration solutions at \(\alpha = 0.6\) in 0.1 N NaCl solutions. As in Fig. III.2 and III.3, the equilibrium surface tension decreases with increasing polymer concentration except at \(C_p = 8.815\) g/l confirming the concentration value for liquid crystal
formation. The time to reach $\gamma_\infty$ is longer at $\alpha = 0.6$ (Fig. III.4) than at $\alpha = 0.95$ (Fig. III.3). Potentiometric studies have shown that xanthan has a helix structure at $\alpha = 0.6$ and a random coil at $\alpha = 0.95$ (Young et al., 1986). Therefore we can conclude that the rate of adsorption of the random coil xanthan form is faster. Most probably the random coil structure has a higher rate of molecular collisions with the surfaces. This observation agrees with the lysozyme adsorption study by Adams et al. (1971). They found that the adsorption of the heat denaturated protein is faster than that of the native protein.

The effects of the degree of ionization, salt concentration and polymer concentration on the equilibrium surface tension can be summarized by plotting $\gamma_\infty$ versus the logarithm of the xanthan concentration (Fig. III.5). $\gamma_\infty$ does not only decrease by adding salt, but also by increasing the degree of ionization. It shows that the random coil structure ($\alpha = 0.95$) is more surface active than the helix structure ($\alpha = 0.6$). It has been reported that the interfacial adsorption of protein will cause structure unfolding (Shirokova et al., 1981; Graham and Phillips, 1979a,b). However, Loeb and Baier (1968) have suggested that protein molecules can partially maintain their secondary structure at interfaces. Most probably then, at $\alpha = 0.6$, xanthan adsorbed at interfaces is either a mixture of native and extensively unfolded molecules, or of molecules in various degrees of unfolding. Therefore, the segments of the molecular chain which contact with surface that results in adsorption must be less than that of random
coil structure. The same result was obtained by Adams et al. (1971) on their study on proteins.

Figure III.5 shows a linear relationship between the $\gamma$ and logarithm of xanthan concentration at all three conditions. This result agrees well with the Gibbs equation (Hiemenz, 1977) which can be expressed as:

$$\Gamma = \frac{-1}{2.303 RT} \frac{d\gamma}{d\log C}$$

where $\Gamma$ is the surface excess of the solute, i.e. the concentration difference between the solute at the surface and the solute in the bulk phase, R is the gas constant and T is the absolute temperature.

The following values were calculated using the data from Fig. III.5:

- $\Gamma_1 = 8.32 \times 10^{-11}$ mole cm$^{-2}$; xanthan in distilled water, $\alpha = 0.95$
- $\Gamma_2 = 1.57 \times 10^{-10}$ mole cm$^{-2}$; xanthan in 0.1 N NaCl, $\alpha = 0.6$
- $\Gamma_3 = 1.18 \times 10^{-10}$ mole cm$^{-2}$; xanthan in 0.1 N NaCl, $\alpha = 0.95$

At the same xanthan solution concentration larger surface excess values means that larger amount of solutes are adsorbed at the surface. $\Gamma_3 > \Gamma_1$ would then explain why the equilibrium xanthan surface tension ($\alpha = 0.95$) decreased in the presence of salt. $\Gamma_2 > \Gamma_3$ reveals that the amount of adsorbed molecules with helix structure is higher than that of the random coil. However, the surface tension of the random coil structure is much lower than that of helix structure. This may suggest that the surface tension depends on the total proportion of molecular segments.
adsorbing at the surface rather than on the number of molecules and that the random coil structure is more flexible and facilitates molecular surface spreading. Therefore, that the total proportion of segments in contact with the interface is much higher for the random coil molecule, and explains the observed lower surface tension measurements. Further studies are needed to confirm this observation. An X-ray fluorescence method has been suggested by Bloch (1985) to study the conformation at polymer-solution-air interfaces.
Summary

The initial surface tension of xanthan solution is only slightly affected by ionic strength, temperature and xanthan concentration. However, the equilibrium surface tension and the adsorption rate of xanthan solutions significantly decrease by increasing xanthan concentration, adding 0.1 N NaCl and increasing the degree of ionization. This suggests that the surface tension depends on the amount of solutes adsorbed at the interface, the electrostatic potential of the polyelectrolyte and the conformation of the polyelectrolyte. The liquid crystal formation can be detected by surface tension measurements. The lower equilibrium surface tension of xanthan solutions suggests that xanthan can be used as a emulsion stabilizer.
Acknowledgment

The authors deeply appreciated the helpful advice from Dr. H.H. Wickman and the use of his laboratory facilities.
<table>
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<tr>
<th>Xanthan Concentration x 10^3 (equivalent/1)</th>
<th>0.8815</th>
<th>2.2038</th>
<th>4.4075</th>
</tr>
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<tbody>
<tr>
<td>NaCl (N)</td>
<td>γ₀ (dyne/cm)</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>69.825</td>
<td>73.059</td>
<td>73.898</td>
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a Drop weight method
Table III.2. Initial dynamic surface tension ($\gamma_0$) of xanthan solution at different degree of dissociation ($\alpha$).

<table>
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<tr>
<th>$\alpha$</th>
<th>0.20</th>
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<th>0.60</th>
<th>0.80</th>
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<tr>
<td>xanthan concentration $\times 10^3$ (equivalent/1)</td>
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<td></td>
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<td></td>
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</tr>
<tr>
<td>0.8815</td>
<td>71.186</td>
<td>69.850</td>
<td>69.897</td>
<td>70.038</td>
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<td>4.4075</td>
<td>75.109</td>
<td>74.835</td>
<td>74.916</td>
<td>73.769</td>
<td>73.898</td>
</tr>
</tbody>
</table>
Table III.3.  Initial dynamic surface tension, $\gamma_0$, of a xanthan solution ($C_p = 0.8815 \times 10^{-3}$ equivalent/l) at different salt concentrations and temperature

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
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<th>50</th>
</tr>
</thead>
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<tr>
<td>Salt Concentration (N)</td>
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<td></td>
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<tr>
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<td>0.25</td>
<td>68.928</td>
<td>67.035</td>
<td>66.358</td>
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Figure III.1  Schematic representation of the drop weight apparatus
Figure III.2  Time dependency of surface tension measurements of different xanthan concentration solutions (α = 0.95)

Concentrations of xanthan solution (equivalent/l):

- □, $8.815 \times 10^{-4}$;
- +, $2.204 \times 10^{-3}$;
- ◇, $4.408 \times 10^{-3}$;
- △, $6.611 \times 10^{-3}$;
- X, $8.815 \times 10^{-3}$.
Figure III.3  Time dependency of surface tension measurements of different xanthan concentration solutions ($\alpha = 0.95$) and 0.1 N NaCl

Concentrations of xanthan solution (equivalent/l):

- □, $8.815 \times 10^{-4}$;
- +, $2.204 \times 10^{-3}$;
- ◊, $4.408 \times 10^{-3}$;
- ∆, $6.611 \times 10^{-3}$;
- X, $8.815 \times 10^{-3}$.
Figure III.4  Time dependency of surface tension measurements of different xanthan concentration solutions ($\alpha = 0.6$) and 0.1 N NaCl

Concentrations of xanthan solution (equivalent/l):
- □, $8.815 \times 10^{-4}$
- ●, $2.204 \times 10^{-3}$
- ◇, $4.408 \times 10^{-3}$
- △, $6.611 \times 10^{-3}$
- ✗, $8.815 \times 10^{-3}$
Fig III.5  Plots of equilibrium surface tension vs. Log Cp (xanthan concentration)

Line conditions: Δ, xanthan in distil. water, α = 0.95; □, xanthan in 0.1 N NaCl, α = 0.6;
○, xanthan in 0.1 N NaCl, α = 0.95.
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