

COMPRESSION DES FILMS INTERFACIAUX ENTRE L'HUILE BRUT ET XANTHAN

COMPRESSION OF INTERFACIAL FILMS BETWEEN CRUDE OIL AND XANTHAN

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RÉSUMÉ

La formation de films interfaciaux possédant certaines propriétés rhéologiques de surface est d'une importance fondamentale pour la stabilité des émulsions dans les pétroles bruts. Le film interfacial formé entre l'huile et l'eau en présence de xanthan a été examiné par la méthode du "bilan de Langmuir" en termes d'isothermes $\pi - A$, sa solidité étant évaluée à partir du travail de compression.

Qu'il soit en poudre ou en liquide fermenté le xanthan a été étudié dissous dans la phase aqueuse pour des salinités variant de 0 à 218 g TDS / l. Une évidente augmentation de la solidité du film interfacial a été observée pour la poudre comme pour le liquide.

La robustesse du film décroît avec l'augmentation de la concentration saline probablement à cause de la réduction de l'activité de surface du xanthan quand celui-ci se stabilise globalement en une structure ordonnée. Par contre, une augmentation de la température jusqu'à 323 K conduit généralement à un renforcement du film et ce en total avec l'évolution de l'activité de surface de xanthan à des températures élevées.

Les isothermes observés sont à la fois du type xanthan, huile et solution saline aqueuse.

ABSTRACT

Formation of interfacial films possessing surface - rheological properties is of fundamental importance for the stability of crude oil emulsions. The interfacial film formed between crude oil and water in the presence of xanthan has been examined using a Langmuir balance in terms of $\pi - A$ isotherms. The strength was evaluated from the work of compression. Both xanthan powder and broth was examined dissolved in the aqueous subphase with salinities from 0 to 218 g TDS/l. An obvious increase in the strength of the interfacial film was observed for broth and powder. This strength decreased with increased salinity probably due to a reduction in the surface activity of the xanthan, as it becomes stabilized in the ordered conformation in the bulk.

Isotherms were observed to be related to both xanthan type, oil and salinity. An increase in the bulk temperature up to 50 °C leads in general to an increase in the film strength in agreement with the rise in surface activity of xanthan powder at elevated temperature.

1 Introduction

A procedure to improve oil production involves the changing of the viscosity of the water phase by adding polymers to obtain the same viscosity as the crude oil to be displaced. Due to the salt stability DEE was quite successfully applied the biopolymer xanthan in its field projects (1). Nevertheless, with increasing oil production strong oil - in - water emulsions occurred which made the separation of the different phases more difficult. The size of the oil drops in the emulsion was on the average 2 to 6 μm . In order to understand the increased stability of the emulsions interfacial film compression measurements were performed to examine effects of temperature, salinity and xanthan composition.

2 Experimental

2.1 Methods

The compression experiments using the Langmuir trough and the Wilhelmy balance were performed as described elsewhere (2). Compressions were performed from 100 to 25 % of the initial surface area (320 cm^2) at a speed of $40 \text{ cm}^2 / \text{min}$. Temperatures between 20 and ca. $50 \text{ }^\circ\text{C}$ were investigated. The subphase was either distilled water or brine with 500 ppm xanthan. 0,10 ml oil was spread on the surface. Surface tension were measured by the Wilhelmy method. Surface pressure vs. fractional area curves were recorded.

2.2 Materials

Three industrial xanthan powders with different pyruvate (P) and acetate (A) content, and molecular weight (MW) were investigated. X1: P, 4,6 %, A, 6,6 %, MW $10,9 \text{ E}06 \text{ g/mol}$. X2: P, 1,9 %; A, 4,6 %; X3: P, 3,1 %, A, 6,0 %, MW, $8,8 \text{ E}06 \text{ g/mol}$. (X3 may contain dispersant agent) (3).

Two systems of different oil and brine composition designated GD and VK were investigated. The oil composition is in % (w/w): Dispersions: GD: 88.4, VK 98.5; Resins: GD 5.5, VK 0.2; Asphaltenes: GD 6.1, VK 1.3; Saturates: GD 36.0, VK 76.1; Aromatics: GD 36.2, VK 22.4; Polars: GD 27.8, VK 1.5; Viscosity (mPas, 20°C) GD 1200, VK 27. Hence GD is an aromatic and VK a paraffinic crude oil. The reservoir brines of TDS 3 (GD) and 218 (VK) g/l contained: NaCl: GD 2, VK 190 g/l; Ca: GD 0.2, VK 5 g/l

A xanthan fermentation broth was also shortly investigated in distilled water and 50 g/l NaCl / l using another oil. An oil soluble demulsifier was added to this.

3 Results and discussion

The results indicates that the formation of an interfacial film responsible for increased emulsion stability is due to an adsorption of both oil and xanthan components. Hence there may also occur interactions between components from each side of the interface. Salinity will effect both the oil component and xanthan adsorption.

3.1 Interfacial Tension

The change in surface tension by the addition of oil to the surface was examined at elevated temperature (GD: 65, VK: $56 \text{ }^\circ\text{C}$). Both systems were stable before and after addition of the oil. The change in γ was fast and unaffected by salinity. γ was 56 and 13 mN / m for respectively GD and VK oil. In the presence of xanthan γ was not stable. This may be due to a short heating time and an increased disorder with time. This could be the explanation for a decrease in γ with time. In addition of oil the change in γ was fast but mostly did not lead to a stable condition. Based on this long heating times were used in the below $\pi - A$ measurements as well as lower temperatures.

As reported previously the surface tension of xanthan solutions increases with increasing temperature (3).

3.2 $\pi - A / A_0$ Isotherms

The strength of the interfacial film was evaluated by interaction of the isotherms thereby obtaining the work of compression (W_c) of the film. W_c is related to the amount and extension of adsorption at the interface (2).

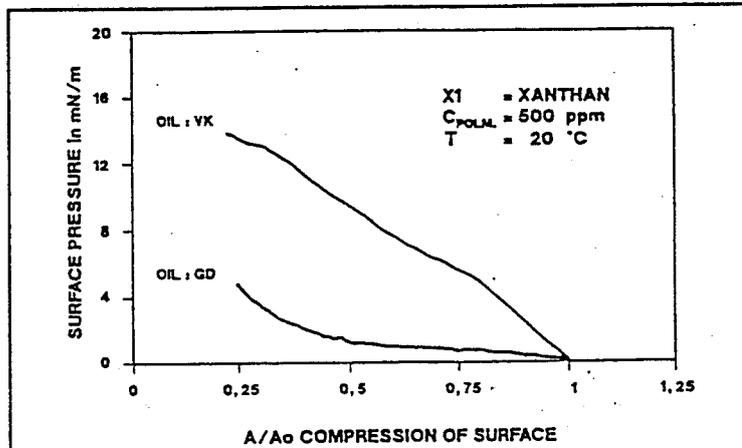


Fig. 1: Surface pressure as a function of compression for GD- and VK-oil at 20 °C in de mineralised water

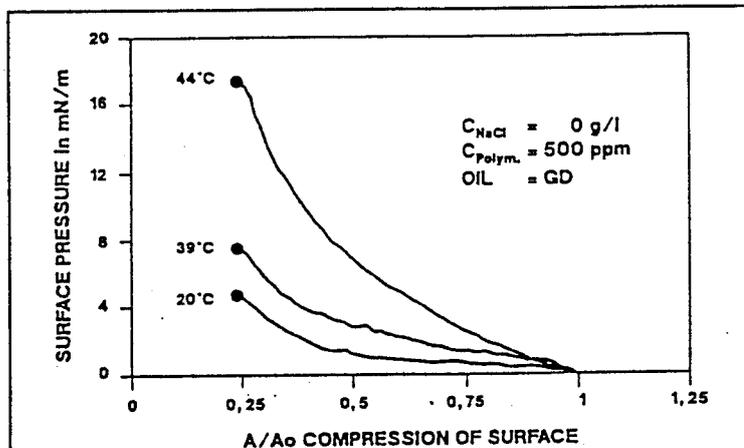


Fig. 2: Surface pressure at different temperatures for GD-oil/xanthan solution in de mineralised water

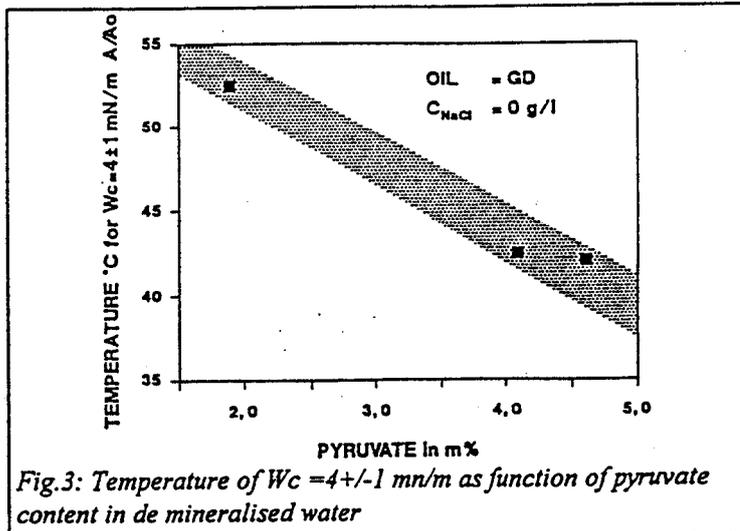


Fig.3: Temperature of $W_c = 4 \pm 1$ mN/m as function of pyruvate content in de mineralised water

In all cases coalescence of the spread oil film was seen close to the 0.25 compression. No large relaxation was seen hence the interfacial film is stable. Figure 1 shows the difference between isotherms when using either VK or GD oil on distilled water. The latter indicates a gas - like state in the initial part of the compression, whereas the VK curve indicates a liquid state. With increasing temperature π increases on distilled water (Figure 2). A pronounced difference between products were found: as the pyruvic content increased so did π and W_c . The results from the three xanthans are given in Table 1. From these a relation between T and W_c was estimated and the temperature T_4 at $W_c = 4$ mN / m was calculated. As the pyruvic content increases T_4 decreases, Figure 3. For GD systems the effect of temperature is reversed on brine, whereas the effect seen for VK is small. The latter is ascribed to the high salinity of VK brine. The electrostatic repulsion between pyruvate groups is diminished as the ionic strength increases, leading to a change in surface behaviour. The X2 xanthan acts differently compared to

Table 1: Work of compression (W_c) of oil/xanthan solutions in brines at 20 and 45 °C

| XANTHAN | OIL : GD | | | | OIL : GD | | | PYRUVATE m % |
|---------------|-------------------------------|------|---------------------------|------|-----------------------|---------------------------|------|-----------------|
| | DEMIN. WATER 20° C 45° C | | GD BRINE 20° C 45° C | | DEMIN. WATER 20° C | VK BRINE 20° C 45° C | | |
| X1 | 0,94 | 4,12 | 4,45 | 1,41 | 5,93 | 4,09 | 4,26 | 4,6 |
| X2 | 1,00 | 3,53 | 2,94 | 7,20 | 6,06 | 5,03 | 4,04 | 1,9 |
| X3 | 1,36 | 5,00 | 3,54 | 2,31 | 4,63 | 5,53 | 3,17 | 4,1 |
| NO XANTHAN | 0,78 | 3,00 | | | 3,70 | | | |

$W_c = \text{mN/m}$

Table 2: Xanthan in de mineralised water and GD-oil. Effect of temperature on W_c , π and γ in mN/m

| XANTHAN | °C | W_c | π | γ |
|---------|------|-------|-------|----------|
| X1 | 20 | 0,936 | 4,74 | 57,44 |
| | 39 | 1,875 | 7,45 | 56,13 |
| | 42,7 | 4,118 | 17,30 | 50,58 |
| | 45,6 | 7,230 | 26,55 | 54,73 |
| X2 | 20 | 0,993 | 5,43 | 49,43 |
| | 48 | 2,022 | 11,93 | 53,90 |
| | 52,8 | 3,525 | 16,53 | 55,05 |
| X3 | 20 | 1,359 | 9,97 | 54,83 |
| | 42,2 | 5,003 | 23,38 | 55,75 |

X1 and X3. The increased salinity when going from GD brine leads to an increase in π for X1 and X3 but a decrease for X2 at both 20 and ca. 45 °C. This is also seen in W_c for air / solution interfaces. X2 has a very low pyruvate content compared to X1 and X3.

When oil is added to the surface W_c increased for all xanthans at 20 °C. Around 45 °C the changes were more complex and may be related both to a partial unfolding of the xanthan molecule leading to an increased interaction with ions and to the oil / water interfacial tension dependence on oil composition. The data indicate that the apparently paraffinic VK oil forms a far stronger film than does the aromatic GD oil. W_c is about five times larger for VK relative to GD oil at distilled water. This indicates that natural

surfactants in VK are more active than those present in GD. Selected W_c results are given in Table 2 indicating the complexity of the film formation when both oil, salinity and temperature is altered.

3.3 Xanthan Broth Systems

Using broth based xanthan a remarkable surface tension lowering has been observed due to the presence of other surface active components in the broth (4). W_c was much larger than for the powder systems and it was found that larger amounts of demulsifier were needed to de stabilise the interfacial film in the presence of xanthan broth. Solutions were 200 ppm active xanthan. For this system salinity was found to diminish W_c in agreement with the above presented results (Figure 4).

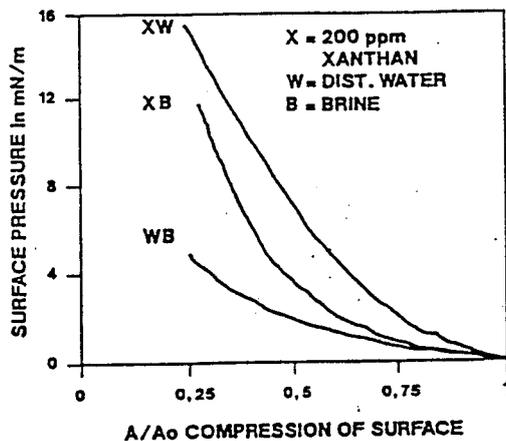


Fig.4: Effect of xanthan in de mineralised water and brine on surface pressure

4 Conclusions

The presence of xanthan was found to increase the strength of the interfacial film between crude oil and water, hence leading to an increased emulsion stability. In distilled water an increased film strength was determined with increasing temperature due to an increased surface activity. This is explained by a partial unfolding of the xanthan conformation. The activity is increased by increasing pyruvic (P) content. An estimated transition temperature T4 was found to decrease with increasing P. For brine systems a far more complex picture emerged as interaction between the ions and the carboxylic groups of the xanthan may dominate.

Based on the above work it is concluded that both oil and xanthan components take part in the formation of interfacial films leading to increased emulsion stability.

5 References

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