ENORDET SURFACTANTS FOR ENHANCED OIL RECOVERY
Producing more from your current operations

Shell Chemicals
When an oil field reaches the end of its normal life, the bulk of its oil (on average two-thirds) remains in the ground because it is too difficult or too expensive to extract it. Estimates suggest that recovery of an additional 1% throughout the world would make the equivalent of 88 billion barrels of additional oil available.

Enhanced Oil Recovery (EOR) techniques aim to extract more crude oil from reservoirs. Normally, when primary and secondary oil recovery techniques have been employed, 60 - 70% of the oil originally in place is left behind. EOR, or tertiary recovery, can extract a large part of that remaining oil. This has the benefits of continued use of existing infrastructure, increased investment and jobs in local economies. It is also responsible stewardship of oil that has already been discovered whilst minimising the impact on the environment.

EOR encompasses a range of techniques that inject steam, gas or water into the oil reservoir. Although still experimental, research suggests that the effectiveness of these techniques can be further improved by employing specific detergents and other additives. Shell Chemicals has developed such detergents (or surfactants) and has large scale manufacturing capabilities that offer long-term supply security. These ENhanced Oil Recovery DETergents are offered under the ENORDET brand name.

ENORDET surfactants can be dissolved in fresh or saline water together with polymer (SP-flood) and alkali (ASP-flood) and injected into the oil reservoir to increase oil recovery. (A)SP flooding might be a logical extension of your existing water flood.

To obtain the best results possible, the (A)SP formulation should be tailored to the crude oil and reservoir conditions. Shell Chemicals can support you in the formulation process and advise you as you determine which combination of surfactants gives optimum performance for your field.
**WHY DO BUSINESS WITH SHELL?**

**CUSTOMER SUPPORT**
We can support our customers in their (A)SP formulation efforts and help them develop a surfactant combination that results in an ultra-low interfacial tension (IFT) with their crude, which is essential for good oil recovery. Crude-oil parameters such as total acid number (TAN) and viscosity, as well as brine composition (salinity, presence of di-valent ions such as Ca and Mg) must be taken into account when formulating. The particular reservoir conditions, such as temperature, permeability and rock type, as well as practical considerations, such as the availability of fresh water or softened (saline) water, should be discussed. Core-flood performance testing, employing the customer’s crude-oil and brine under the prevailing reservoir conditions, can be offered.

Additional practical considerations that should be included are the constraints posed by the location. For example off-shore locations often pose constraints on storage space, weight and available power.

**PRODUCT RANGE AND INNOVATION**
Shell Chemicals offers a range of ENORDET surfactants which by careful formulation can match diverse crudes and reservoir conditions. Technical developments focus on further extending the range of surfactants to match wider ranges of salinities and temperatures, thereby enabling the (A)SP technology to be deployed in even more demanding fields.

To facilitate supply and minimise on-site storage space requirements, we are developing improved means of shipment of our surfactants, e.g. by providing highly concentrated liquids, pastes and powders.

**LOGISTICS**
We serve customers globally; products can be shipped using marine vessels, barges, railroad and trucks. Smaller quantities can be arranged in IBC or drums for small-scale pilot testing. Wherever your oilfield is located, Shell Chemicals can deliver the product you need in the quantities you require.

**HEALTH, SAFETY & THE ENVIRONMENT (HSE)**
All HSE regulations must be met during manufacture, transport, storage and use of our ENORDET products. Shell Chemicals fully complies with all applicable regulation and is committed to ensure that all our products are produced, transported, stored and applied in a responsible way. Dedicated HSE experts, who work in close collaboration with industry HSE networks, can support ENORDET customers in meeting their HSE requirements.

**QUALITY ASSURANCE & QUALITY CONTROL (QA/QC)**
Shell manufactures products according to the highest industry standards. We have full QA/QC processes in place to ensure our customers receive the quality product they need. Our plants are ISO 9001 and ISO 14001 certified.
Scaling up surfactant quantities: support from lab to full field application.

**Phase Behaviour**
low cost grams

**Core Flow**
kilograms

**SINGLE WELL TEST**
500–3000 kg

**CORE**
Porosity = 0.25

**EOR SLUG**
20–feet

**EOR SLUG**
Oil

**COMMERICAL OPERATION**
20–50 kilotons pa

**MULTIPLE WELL FIELD TEST**
0.5–5 kiloton

**Scaling up Surfactant Quantities:** From Lab to Full Field Application.
HOW ARE ENORDERT ENHANCED OIL RECOVERY SURFACTANTS USED?

In surfactant-based enhanced oil recovery, the oil reservoir is flooded by pumping in water containing a small percentage (typically 0.3 – 1%) of surfactant. The surfactant overcomes natural capillary forces by lowering the crude oil/water interfacial tension (IFT) to an ultra-low level. This allows oil globules in the reservoir to flow through rock pores and coalesce to form a clean oil bank.

To achieve this effect, specific ENORDERT surfactants must be selected and matched to specific reservoir conditions:
- temperature of the reservoir
- water salinity and divalent ion concentration (water hardness)
- crude oil type (viscosity, TAN, etc.)

Selection of the correct surfactants is important to prevent the formation of viscous emulsions which can prevent effective transport of the surfactant solution (and oil bank) through the reservoir. Alkali is often added to the aqueous surfactant solution to increase efficiency, as it helps to reduce surfactant adsorption to the rock.

In the case of high TAN crude oils, alkali generates additional soaps through reaction with naturally occurring acids in the crude oil. A water-soluble polymer such as partially hydrolysed polyacrylamide (HPAM) is usually added to increase the viscosity of the water phase and improve mobility control.

The alkali surfactant polymer (ASP) slug is usually followed by a slug of polymer solution (polymer drive) that acts as a piston to push the oil bank through the reservoir to the producing wells.

Individual ENORDERT grades can be blended to match a particular reservoir salinity. Synergistic effects are usually observed when combining internal olefin sulphonates (IOS) with alcohol alkoxy sulphates (AAS) type of surfactants.
A RANGE OF ENORDET GRADES TO MATCH YOUR RESERVOIR

KEY DATA FOR POPULAR ENORDET SURFACTANTS

<table>
<thead>
<tr>
<th>ENORDET™ surfactant type</th>
<th>CARBON NO. CHAIN LENGTH</th>
<th>APPLICABLE SALINITY*</th>
<th>PO/EO PER ALCOHOL UNIT (mol/mol)</th>
<th>APPLICABLE TEMPERATURE RANGE **</th>
<th>DI-VALENT ION TOLERANCE #</th>
</tr>
</thead>
<tbody>
<tr>
<td>O242 IOS C20-24</td>
<td>low/med</td>
<td>none</td>
<td>ambient to 200°C</td>
<td>limited</td>
<td></td>
</tr>
<tr>
<td>O323 IOS C15-18</td>
<td>high</td>
<td>none</td>
<td>ambient to 200°C</td>
<td>limited</td>
<td></td>
</tr>
<tr>
<td>O342 IOS C19-23</td>
<td>medium</td>
<td>none</td>
<td>ambient to 200°C</td>
<td>limited</td>
<td></td>
</tr>
<tr>
<td>O352 IOS C24-28</td>
<td>low</td>
<td>none</td>
<td>ambient to 200°C</td>
<td>limited</td>
<td></td>
</tr>
<tr>
<td>A771 AAS C16-17</td>
<td>low/med</td>
<td>7 PO</td>
<td>ambient to ≥60°C</td>
<td>excellent</td>
<td></td>
</tr>
<tr>
<td>A031 AAS C16-17</td>
<td>medium/high</td>
<td>3 EO</td>
<td>ambient to ≥60°C</td>
<td>excellent</td>
<td></td>
</tr>
<tr>
<td>J771 AAS C12-13</td>
<td>low/med</td>
<td>7 PO</td>
<td>ambient to ≥60°C</td>
<td>excellent</td>
<td></td>
</tr>
<tr>
<td>J1111 AAS C12-13</td>
<td>low/med</td>
<td>11 PO</td>
<td>ambient to ≥60°C</td>
<td>excellent</td>
<td></td>
</tr>
<tr>
<td>J13131 AAS C12-13</td>
<td>low/med</td>
<td>13 PO</td>
<td>ambient to ≥60°C</td>
<td>excellent</td>
<td></td>
</tr>
<tr>
<td>J071 AAS C12-13</td>
<td>very high</td>
<td>7 EO</td>
<td>ambient to ≥60°C</td>
<td>excellent</td>
<td></td>
</tr>
</tbody>
</table>

IOS: internal olefin sulphonate, AAS: alcohol alkoxy sulphate. More detailed chemical structures can be found in Shell papers published in the SPE conference proceedings, e.g. SPE 113313, Development of Surfactants for Chemical Flooding at Difficult Reservoir Conditions.

* the range of salinities where a surfactant can be applied is formulation dependent
** up to 60°C for SP formulations, slightly higher for ASP formulations
# effective di-valent ion tolerance is formulation dependent

The ‘applicable salinity’ column is for guidance only. A target optimal salinity can be achieved through blending surfactants to match the crude and reservoir conditions. For example, ENORDET O332 can be used both in medium and high salinity environments when combined with other ENORDET surfactants.

Please note that this table is not exhaustive; other grades are available upon request, e.g. when your reservoir demands even higher salinity surfactants.

Additionally, alpha olefin sulphonates (AOS) are available. AOS and alkyl aryl sulphonates were developed as foaming agents and Shell Chemicals can supply the raw materials as well as arrange the manufacture of these products.

This table does not include co-solvents or aqueous solubilisers. Several of Shell’s NEODOL alcohol ethoxylates can function as solubiliser to improve aqueous solubility of the main surfactants and to reduce micro-emulsion viscosity. See also co-solvents and aqueous solubilisers.
CO-SOLVENTS AND AQUEOUS SOLUBILISERS

Co-solvents are often required for ASP or SP formulations to improve aqueous solubility and reduce micro emulsion viscosity. Typical co-solvents are SBA and IPA, both low molecular weight alcohols.

Shell’s NEODOL alcohols and alcohol ethoxylates are superior solubilisers. The main advantage they offer over low molecular weight alcohols is being effective at much lower concentrations, thereby reducing logistics costs. They also have lower volatilities thus minimising HSE hazards. See also the SPE paper by the University of Texas: SPE130007, “The Role of Co-Solvents and Co-surfactants in Making Chemical Floods Robust”.

Please see our website for more extensive information on NEODOL products: www.shell.com/chemicals/neodol

CONCENTRATED ENORDET SURFACTANTS

From a logistics and operational point of view, it is desirable to ship concentrated surfactants as it minimises transport costs and reduces required storage space. Depending on concentration and surfactant type, the ENORDET surfactants range in physical properties from (low viscosity) liquids to higher viscosity pastes.

BLENDS

To simplify field operations, it may be desirable to ship the surfactant system as a concentrated blend rather than ship the single surfactants; this has the advantage of only requiring one surfactant storage tank and no need for a surfactant mixing process at site. An additional benefit is that a combination of IOS and AAS surfactants often results in a (lower viscosity) liquid, also at high concentration, which improves handleability compared to a paste.

When preferred, Shell Chemicals can develop a customer-specific, concentrated blend. Various factors should be taken into account. These include: local conditions such as prevailing climate, storage options, logistic challenges (e.g. off-shore supply), modes of shipment, and finally dissolution of the product into the water stream to be injected. Given the many possibilities, blend development should be carried out in close collaboration with the customer.

We continue to develop even more cost-effective and safe transport and storage solutions. An example is the development of surfactant powders.
The (A)SP process uses a fluid mixture that comprises more than 97% water, which may be obtained from various sources, including co-produced water (saline, non-potable water).

The ASP ingredients are comparable to common household products:

- **Alkali**, typically sodium carbonate (also known as “washing soda” or “soda ash”), is used in ASP mixtures:
  - The concentration of alkali is usually between 1% and 2%,

- **Surfactants**
  - The concentration of surfactants in the (A)SP mixture is usually between 0.3% and 1%,
  - The surfactants are similar, but not identical, to those found in many products we use every day: shampoo, laundry detergent, dishwashing soaps etc.

- **Polymers**
  - The concentration of polymers in the (A)SP mixture is usually between 0.1% and 0.3%,
  - The polymer used is partially hydrolysed polyacrylamide (HPAM). HPAM polymers are used in many water treatment and purification applications, and also in nappies.
SECURITY OF SUPPLY

We offer reliable supply with the scale to grow with your business. Collectively, Shell chemicals companies are the largest global producers of olefins, alcohols and alcohol alkoxylates, which form the feedstock for the ENORDDET product range. We manufacture both in the US (3 units, Geismar, Louisiana) and in the EU (1 unit, Stanlow, UK).

CUSTOMER SERVICE

We have sales and customer centre teams on six continents available to recommend products and help you develop optimal supply solutions. Experienced staff based in Houston and Amsterdam also provide dedicated technical support. You can reach us via our webpage (www.shell.com/chemicals/enordet) or directly by contacting our customer service centre.

QUALITY

Plants are ISO 9001 and ISO 14001 registered, and we continuously monitor our processes from feedstock unloading through product delivery.

HSE AND PRODUCT STEWARDSHIP

Shell chemicals companies are proactive in global health, safety and environment arenas. Our HSE experts can provide training and appraisals in the proper handling and use of our products.
ELECTRONIC INTERFACES

Shell Chemicals offers a variety of eBusiness solutions to make ordering and managing your ENORDET inventory quick and easy. The Customer Lounge is a secure web-based interface where you can place, track and manage product orders. Through the transaction network Elemica™, electronic trading is made more efficient via standardised processes.

ON THE WEB

Shell Chemicals gives access to years of technical development behind the ENORDET products on our website: [www.shell.com/chemicals/enordet](http://www.shell.com/chemicals/enordet).

Information downloads in PDF format include datasheets, technical papers, MSDS and safety literature.
SURFACTANTS FOR EOR

SURFACTANT

Surface Active Agent, a chemical (effectively a soap) designed to lower the interfacial tension (IFT) between oil and water. The IFT is typically lowered from 30 – 40 mN/m (dyne/cm) to values of <0.001 mN/m. At this extremely low IFT, micro-emulsions tend to form which are thermodynamically stable. Low viscosity micro-emulsions are required to minimise surfactant losses within the reservoir and the selection of surfactants is critical to facilitate this.

ALKALINE SURFACTANT POLYMER FORMULATION

Effective transport of the aqueous solution (and oil bank) through the reservoir is the key to successful surfactant-based EOR and this is achieved through the design of an optimised formulation.

A water-soluble polymer such as partially hydrolysed polyacrylamide (HPAM) is usually added to increase the viscosity of the water phase to improve mobility control.

Alkali is often added to the aqueous solution to increase efficiency as it helps to reduce surfactant adsorption to the rock. In the case of ‘high TAN’ crude oils, alkali also generates additional surfactants through reaction with the acids present. These surfactants aid in the generation of an ultra-low IFT between the oil and water.

PHASE BEHAVIOUR TEST

To test the ability of certain surfactant formulations to generate an ultra-low IFT and form a micro-emulsion between a particular crude and the injected brine, a set of test tubes are filled with ASP solution and crude. The contents are mixed well and observed over time whilst they are kept in an oven at the reservoir temperature. Each test tube has a different salinity thus providing a salinity scan. The salinity at which the largest volume of micro-emulsion develops as a middle phase has the highest potential for that particular ASP formulation.

Selected formulations are further tested in core-flood experiments which simulate fluid propagation and oil recovery in the reservoir.

Disclaimers

Shell Chemicals refers to the various Shell Group companies engaged in the chemicals business. The Shell Group refers to the companies in which Royal Dutch Shell plc. directly or indirectly owns investments. Each of the companies that make up the Shell Group of companies is an independent entity and has its own separate identity.

The information contained in this publication is to the best of our knowledge true and accurate, but any recommendations or suggestions that may be made are without guarantee since the conditions of use are beyond our control. Furthermore, nothing contained herein shall be construed as a recommendation to use any product in conflict with existing patents covering any material or its use.

ENORDET, NEODENE, NEODOL and NEOFLO are trademarks of the Shell Group of companies.

Please go to our website www.shell.com/chemicals/enordet to contact us.

Published April 2013. All rights reserved.

The copyright of this document is vested in Shell Chemicals Europe B.V., Rotterdam, The Netherlands. All rights reserved. Neither the whole nor any part of this document may be reproduced, stored in any retrieval system or transmitted in any form or by any means without the prior written consent of the copyright owner.