DOCTORAL (PhD) DISSERTATION THESES

STUDY ON SURFACTANT BLEND PRODUCED FOR PETROLEUM INDUSTRY PURPOSES

PREPARED WITHIN THE FRAMEWORK OF THE DOCTORAL SCHOOL OF CHEMICAL ENGINEERING AND MARTERIAL SCIENCES

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1 Introduction and Objectives

Nowadays, increasing emphasis is being placed on the research of renewable and sustainable energy sources, and on the goal of reducing the reliance on fossil fuels. However, crude oil—as both an energy source and a raw material—is expected to continue playing a significant role in the coming years. Since crude oil is a finite energy resource and raw material, research and methods aimed at improving extraction efficiency are comeing tot he fore. These include surfactant and surfactant-polymer flooding reservoir recovery techniques. The application of such methods is becoming increasingly necessary even under challenging reservoir conditions, such as high-salinity formation waters or high-temperature reservoirs.

The applicability of surfactants and surfactant compositions is increasingly limited by tightening environmental regulations, which necessitate the development of new, environmentally friendly surfactants made from green raw materials, instead of previously effective surface-active agents. However, these new surfactants generally have a narrower range of applicability. With the expansion of available surfactant types and the extreme reservoir conditions, previously unobserved phenomena and new challenges are emerging, making the custom development of surfactant compositions necessary. These new challenges and solutions also call for the reconsideration of previously applied development processes and measurement methods.

The aim of my PhD research is to review and further develop the testing methods used in the development and selection of surfactants and surfactant compositions. For those testing methods where improvement is required, I intend to enhance the reliability of the tests and/or reduce health and safety risks associated with their execution. Additionally, my goal is to uncover correlations that facilitate the development of surfactant compositions by examining how modifications in composition affect key performance characteristics.

2 Experimental Work

In the first part of my experimental work, I carried out the further development of three testing methods commonly used in surfactant development.

The determination of the water number is a property associated with the hydrophilic-lipophilic balance of surfactants. This test traditionally requires a mixture of cyclohexane and 1,4-dioxane as organic solvents. In my work, I replaced the latter component to reduce the health risks associated with the test.

The method used to examine the oil-washing efficiency of surfactants and surfactant compositions is a quick and simple test, serving as a tool for the preliminary selection of surfactant formulations. In the original method, the reservoir rock layer is created using chloroform as a solvent. However, this approach results in a fragile rock layer. As part of my PhD research, I improved the method by modifying the geometry of the rock layer used in the test. In the new method, the rock layer is formed inside a glass capillary, making it less prone to damage. Another advantage of the new method is that it does not require organic solvents for the preparation of the layer, which reduces both the cost and the health risks of the test.

The third method I considered necessary to improve was the emulsion stability test. This test is widely used around the world, yet there are minor variations in its execution that prevent the comparability of results between different research institutions. In my work, I examined and demonstrated that mixing intensity is a critical factor in the implementation of this test. By properly selecting this parameter, measurement errors can be significantly reduced.

In the second part of my experimental work, I examined how changes in the composition of surfactant formulations—such as the ratio of the components or the introduction of new ones—affect the solubility and interfacial tension against crude oil in high-salinity formation water environments.

Furthermore, I investigated the effects of varying proportions of oxo-alcohol type solvents on the oil-washing and emulsifying performance as well as on interfacial tension results, both for standalone surfactant compositions and when used in combination with flow-modifying polymers.

Finally, I investigated the rheological properties of surfactant composition solutions by adding a new surfactant component to a previously successful formulation. I also examined how these properties change when the surfactant composition is used in combination with a flow-modifying polymer.

3 New Scientific Results

1 Development of a Method for Evaluating Emulsifying Performance

One of the most widely used methods for selecting surfactant compositions in tertiary oil recovery is the evaluation of emulsifying performance. In the course of my work, I investigated the emulsifying effect of sodium laureth sulfate and coconut fatty acid diethanolamide surfactants, as well as their combinations, in RV-(6) formation water solutions with an active substance concentration of 15 g/L. These were tested with KO-1 crude oil at 25 °C, under varying mixing parameters (mixing time [5–600 sec] and mixing speed [500–1500 rpm]).

a) *The apparatus suitable for the standardized testing of water separation from dairy products and refined petroleum products (ADEM) can also be used for the analysis of crude oil-brine emulsions.*
b) *It was observed that increasing the mixing time and/or mixing speed leads to the formation of a characteristic emulsified phase for the given conditions. Further increases in mixing intensity did not result in significant changes, indicating a saturation point.*
c) *I conducted comparative tests with manually performed emulsifying evaluations. Based on these comparisons, I concluded that emulsifying performance testing carried out with an automated device—when optimal mixing parameters are selected—yields more reliable results than traditional manual emulsifying tests.*
d) *During the reliability assessment of the method, I found that the relative deviation between parallel tests under identical parameters remained below 3%, which represents an improvement in precision compared to existing methods.*

2 Method Improvement for Evaluating Oil Washing Efficiency

The evaluation of oil washing efficiency is a rapid selection method used for surfactant compositions applied in petroleum production. In this test, the type of crude oil, formation water, and rock matrix all influence the outcome. In previously applied methods, the formation layer made of powdered rock core was prepared on a glass plate using chloroform as a solvent. In my work, I reviewed and improved this method.

a) *The oil washing efficiency test can be performed using a glass capillary containing a phase made of powdered rock, prepared without the use of chloroform (or any other solvent).*
b) *Based on reliability testing, the method's relative standard deviation was determined to be below 10%, which is in line with the original method.*
c) *From comparative tests, I found that the correlation factor between the results obtained with the two methods was 0.9907, indicating that the results from both methods are comparable.*
d) *I also studied the effect of the packing density (powdered rock) on the test results in the glass capillary. Within the tested parameter range, a change in packing density between 1.490–2.656 g/cm³ did not affect the results.*

3 Improvement of the Water Number Determination Method

The determination of the water number is a suitable method for characterizing the hydrophilic-lipophilic nature of surfactants. In this method, the surfactant is dissolved in a solvent mixture composed of cyclohexane and 1,4-dioxane. In my work, I replaced the 1,4-dioxane component with acetone for various surfactants (anionic, nonionic, and amphoteric types) used in the petroleum industry within the HLB (hydrophilic-lipophilic balance) range of 7.5 to 17.

a) *In the case of the tested surfactants, the 1,4-dioxane component of the cyclohexane:1,4-dioxane solvent mixture used for determining the water number can be replaced by acetone.*
b) *When evaluating the reliability of the method, I found that the relative standard deviation of the measurements performed with acetone was lower compared to those obtained using the original 1,4-dioxane solvent mixture.*
c) *Comparing the measured water number values with those calculated from literature data, I concluded that the relative error of the measurements using acetone is smaller than that of the tests conducted with 1,4-dioxane.*

4 Investigation of the Solubility of Surfactant Compositions in High-Salinity Formation Water for Surfactant Mixture Development

One of the major challenges associated with the application of surfactant compositions for enhanced oil recovery is their performance in high-salinity hydrocarbon reservoirs. In my work, I examined the solubility of various surfactants—previously proven to be effective in low-salinity formation waters—in high-salinity RV-(245) formation water at 25 °C and at a concentration of 1 g/L. Additionally, I tested the solubility of surfactant compositions prepared from these surfactants and determined their interfacial tension against KO-3 type crude oil.

a) *During the solubility tests in formation water, I found that among the tested surfactants (sodium lauryl ether sulfate, KOMAD-710, KOMAD-711, and Disponil ALS33), only the anionic sodium lauryl ether sulfate showed good solubility under the given conditions. However, when these surfactants were combined with 2-butoxyethanol as a co-solvent in surfactant compositions, even those surfactants that were otherwise poorly soluble or insoluble could be brought into solution under the examined conditions.*
b) *A linear correlation was observed between the turbidity of the surfactant composition solutions—formulated using the same system—and their interfacial tension values against crude oil.*

5 Investigation of the Use of Oxo-Alcohol Type Compounds as Co-Solvents for Surfactant Mixture Development

I studied the effects of 2-butoxyethanol and 2-phenoxyethanol as co-solvents at concentrations ranging from 1 to 15 m/m% in a 90/10 m/m% surfactant composition consisting of coconut fatty acid diethanolamide and Hostapur OS, both without and with the addition of 1 g/L of POL-1 flow-modifying polymer. During my research, I evaluated the emulsification performance at 80 °C after a 24-hour settling period using a 50/50 V/V% mixture of KO-1 crude oil and RV-(6) formation water. Furthermore, I determined the interfacial tension between crude oil and formation water at 40 °C and performed oil-washing efficiency tests using powdered sandstone from Algyő at 80 °C.

a) *The addition of 2-butoxyethanol and 2-phenoxyethanol to the 90/10 m/m% surfactant composition of coconut fatty acid diethanolamide and Hostapur OS decreases the emulsification efficiency.*
b) *Under the tested conditions, the use of 2-butoxyethanol and 2-phenoxyethanol improves oil-washing efficiency and reduces the interfacial tension between crude oil and formation water.*
c) *I found that when 1 g/L of the flow-modifying polymer POL-1 is used, 2-butoxyethanol in the range of 1–3 m/m% and 2-phenoxyethanol in the range of 1–10 m/m% increase the interfacial tension. However, by increasing the co-solvent*

ratio in the surfactant composition, the interfacial tension can be reduced compared to values obtained without the use of co-solvents.

6 Investigation of the Rheological Properties of Surfactant-Polymer Solutions for Surfactant Mixture Development

In enhanced oil recovery processes, beyond the separate selection of surfactant compositions and flow-modifying polymers, it is also necessary to investigate their combined behavior. Based on previous tests, I examined the changes in viscosity as a function of shear rate for a 15 g/L aqueous solution of a surfactant composition prepared from a 70/30 m/m% mixture of KOMAD-711 (anionic) and KOMAD-710 (nonionic) surfactants. To this surfactant composition, I added 25 m/m% sodium lauryl ether sulfate (anionic surfactant), and in the formation water solution, I used flow-modifying polymers with different molecular weights at a concentration of 1 g/L.

a) *When the surfactant composition of KOMAD-711 and KOMAD-710 is used together with a flow-modifying polymer in RV-(6) formation water, a positive interaction is observed between the surfactant composition and the polymer in terms of viscosity in the shear rate range of 1–1000 1/s at 25 °C.*
b) *By adding 25 m/m% sodium lauryl ether sulfate to the surfactant composition of KOMAD-711 and KOMAD-710, the viscosity of the surfactant solution in formation water can be increased.*
c) *A favorable interaction between the surfactant composition (consisting of KOMAD-710, KOMAD-711, and sodium lauryl ether sulfate) and the flow-modifying polymer occurs only within a specific part of the tested shear rate range.*

7 Industrial Applicability of the Results

During my PhD research, I was awarded an industrial scholarship, which allowed me to participate continuously in ongoing industrial projects, as well as in research and development activities. Over this period, we conducted surfactant selection tests for more than 10 oil fields based on reservoir geology and the physicochemical properties of fluids. The main research directions of my dissertation were driven by current industrial challenges, and the results of my investigations have been utilized in industrial applications.

The improvement of the emulsification testing method was prompted by inconsistencies in results between the research groups involved. I concluded that the differences in results stemmed from the methodology previously used (bottle test or manual method), specifically from the variations in mixing intensity. Based on the method I developed, MOL LUB Ltd.'s quality control laboratory acquired suitable testing equipment and integrated the new method into the qualification process for surfactants and surfactant compositions they produce.

There were two main drivers for the development of the oil washing efficiency testing method. First, the use of chloroform in the original method no longer complies with current safety regulations. Second, the original method could not be applied to high-quartz-content powdered rocks, as the thin rock layer would not remain on the glass surface. The improved method addresses the chloroform-related issues by eliminating the need for organic solvents and, due to its modified geometry, allows for testing even with pure quartz sand. Researchers at the University of Pannonia have successfully applied the method for surfactant screening using quartz-based powdered rock material.

One of the greatest current challenges in surfactant composition development is their application in high-salinity formation waters. Surfactants that have proven effective under low-salinity conditions often fail to dissolve—or dissolve only partially—under high-salinity conditions, which significantly reduces their efficiency. In my work, I investigated the applicability of surfactant compositions in such environments. The results were used in several projects aimed at developing surfactant compositions tailored to specific oil field parameters. Following scale-up trials, experts at MOL Plc. incorporated the developed surfactant formulations into the company's product portfolio and production process, resulting in two new commercially available products (KOMAD-6241SD and KOMAD-6241SE).

Several surfactant compositions in MOL Plc.'s portfolio contain 2-butoxyethanol as a component. This solvent has a relatively low closed-cup flash point (67 °C), which complicates its manufacturing, transport, and use—especially during the summer months and in warmer climates. In my research, I explored alternative solvents, which led to the launch of a new Mediterranean surfactant product line by MOL Plc.

8 Publications related to the topic of the doctoral thesis

8.1 Publications forming the basis of the PhD thesis

Publications in foreign languages and published in foreign journals

1. **Hartyányi, M.**, Nagy, R., Bejczi, R., Bartha, L., & Puskás, S. (2025). The Impact of Salt Concentration on the Screening of Surfactant Packages for EOR Applications. *Energy Science & Engineering*. **[Q2; IF: 3,5]**

2. **Hartyányi, M.**, Nagy, R., Bartha, L., & Puskás, S. (2024). Study on Emulsification Effect of Crude Oil in Brine Emulsions by Automated Demulsibility Tester. *Energies*, 17(10), 2438. **[Q1; IF: 3,0]**
3. Nagy, R., **Hartyányi, M.**, Bartha, L., & Puskás, S. (2024). Study On Surfactants Based On Vegetable Oil By Emulsification Effect. *Chemical Engineering Transactions*, *110*, 133-138. **[Q3]**
4. **Hartyányi, M.**, Bejczi, R., Nagy, R., Demcsák, N., Bartha, L., & Puskás, S. (2024). An improved method for determining the water number for surfactants. *MethodsX*, *12*, 102671. **[Q2; IF: 1,7]**

5. **Hartyányi, M.**, Nagy, R., Bartha, L., & Puskás, S. (2024). Investigation the Solubility of Vegetable Oil-based Nonionic Surfactants for the Petroleum Industry. *Chemical Engineering Transactions*, 110, 127-132. **[Q3]**

6. Nagy, R., **Hartyányi, M.**, Bejczi, R., Bartha, L., & Puskás, S. (2025). Recent aspects of chemical enhanced oil recovery. *Chemical Papers*, 1-22. **[Q2; IF: 2,0]**

7. Nagy, R., **Hartyányi, M.**, Bartha, L., & Puskas, S. (2024). Investigation of Interaction Between Viscosity-modifier Polymers and Surfactants Based on Vegetable Oil for Chemical Enhanced Oil Recovery. *Chemical Engineering Transactions*, *109*, 307-312. **[Q3]**

Publications published in Hungarian-language journals

1. **Hartyányi M.**, Nagy R., Bartha L., Puskás S., (2023), Tenzidek emulgeáló hatásának meghatározására alkalmazott módszerek összehasonlító vizsgálata, *Anyagvizsgálók lapja*, 2023/1, 13-16.

International, foreign language conference presentation with full text available:

1. **Hartyányi, M.**, Nagy, R., Bartha, L., & Puskás, S. Investigation the Solubility of Vegetable Oil-based Nonionic Surfactants for the Petroleum Industry; *Industrial Biotechnology International Conference* (Bologna, Olaszország); 2024.06.30-07.04.

2. Nagy, R., **Hartyányi, M.**, Bartha, L., & Puskas, S. (2024). Investigation of Interaction Between Viscosity-modifier Polymers and Surfactants Based on Vegetable Oil for Chemical Enhanced Oil Recovery; *International Conference on BIOMASS* (Palermo, Olaszország) 2024.05. 19-22.

3. Nagy, R., **Hartyányi, M.**, Bartha, L., & Puskás, S. (2024). Study On Surfactants Based On Vegetable Oil By Emulsification Effect. *Industrial Biotechnology International Conference* (Bologna, Olaszország); 2024.06.30-07.04.

International, foreign language conference presentation with abstract publication:

1. **Hartyányi, M.**, Nagy, R., Bartha, L., Puskás, S.; Rheological study on surfactant packages and polymers for chemical enhanced oil recovery; *13. International Colloid Conference* (Sitges, (Barcelona), Spanyolország); 2024.06.09-12.

2. Bejczi, R., **Hartyányi, M.**, Nagy, R., Demcsák, N., Bartha, L., Puskás, S.; Development of Determination Method for the Water Number of Surfactants; *13. International Colloid Conference* (Sitges, (Barcelona), Spanyolország); 2024.06.09-12.

3. Nagy, R., **Hartyányi, M.**, Bartha, L., Puskás, S.; Investigation of stability of surfactant solution for CEOR (Chemical Enhanced Oil Recovery); *13. International Colloid Conference* (Sitges, (Barcelona), Spanyolország); 2024.06.09-12.

4. Nagy, R., **Hartyányi, M.**, Bartha, L., Puskás, S.; Study on the interaction between flow-modifier polymers and surfactants mixtures in chemical enhanced oil recovery; *12th. International Colloid Conference* (Palma de Mallorca, Spanyolország); 2023.05.11-14.

Hungarian-language conference presentation with abstract publication:

1. **Hartyányi, M.**, Nagy, R., Bartha, L., Puskás, S.; Kőolajipari célokra előállított tenzidkompozíciók rétegvízben való oldhatóságának vizsgálata; *XXIX. Nemzetközi Vegyészkonferencia* (Marosvásárhely, Románia); 2023.10.25-28.

2. **Hartyányi, M.**, Nagy, R., Bartha, L., Puskás, S.; Kókuszzsírsav-dietanolamid emulgeáló hatásának vizsgálata a keverés intenzitásának függvényében kőolaj-rétegvíz rendszer esetén; *XXVII. Nemzetközi Vegyészkonferencia* (Online); 2021.10.29.

3. **Hartyányi, M.**, Nagy, R., Bartha, L., Puskás, S.; Emulgeáló képesség összehasonlító vizsgálata; *Műszaki Kémiai Nap 2021* (Veszprém; Online); 2021.04.21.

8.2 Publications related to the topic of the PhD thesis

Publications in foreign languages and published in foreign journals

1. **Hartyányi, M.**, Nagy, R., Bejczi, R., Bartha, L., & Puskás, S. (2025). Estimation of the hydrodynamic diameter of mobility-controlling polymers for chemical enhanced oil recovery based on dynamic viscosity. *Heliyon*, 11(13), e43709. **[Q1; IF: 3,6]**

2. **Hartyányi, M.**, Nagy, R., Bartha, L., & Puskas, S. (2024). Investigation of Vegetable Oil-based Nonionic Surfactants for the Petroleum Industry. *Chemical Engineering Transactions*, 109, 163-168. **[Q3]**

3. **Hartyányi, M.**, Nagy, R., Bartha, L., & Puskás, S. (2022). Selection Method of Flow Modifier Polymers for Chemical Enhanced Oil Recovery. *Acta Materialia Transylvanica (EN)*, 5(1), 14-17.

4. Nagy, R., Kothencz, R., **Hartyányi, M.**, Bartha, L. (2022). Relationship between some Colloidal properties of non-ionic-anionic surfactant mixtures. *Processes*, 10(6), 1136. **[Q2; IF: 3,5]**

5. Nagy, R., Elekes, A., Bartha, L., **Hartyányi, M.**, Puskás, S. (2021). Study on the dynamic viscosity of crude oil-in-water emulsions. *Petroleum Science and Technology*, 39(19-20), 896-907. **[Q3; IF: 1,695]**

6. Nagy, R., **Hartyányi, M.**, Nagy, B., Varga, C. (2020). Determination of free Diethanolamine content. *Papers on Technical Science*, 13, 158-161.

International, foreign language conference presentation with full text available:

1. **Hartyányi, M.**, Nagy, R., Bartha, L., & Puskas, S. (2024). Investigation of Vegetable Oil-based Nonionic Surfactants for the Petroleum Industry. *International Conference on BIOMASS* (Palermo, Olaszország) 2024.05. 19-22.

International, foreign language conference presentation with abstract publication:

1. **Hartyányi, M.**, Nagy, R., Bartha, L., Puskás, S.; New selection method of flow-modifying polymers for chemical enhanced oil recovery; *12th. International Colloid Conference* (Palma de Mallorca, Spanyolország); 2023.05.11-14.

Hungarian-language conference presentation with full text available::

1. **Hartyányi, M.**, Nagy, R., Bartha, L., & Puskás, S. (2022). Selection Method of Flow Modifier Polymers for Chemical Enhanced Oil Recovery. *Acta Materialia Transylvanica (EN)*, 5(1), 14-17.

2. Nagy, R., **Hartyányi, M.**, Nagy, B., Varga, C. (2020). Determination of free Diethanolamine content. *Papers on Technical Science*, 13, 158-161.

Hungarian-language conference presentation with abstract publication:

1. **Hartyányi, M.**, Nagy, R., Bartha, L., Puskás, S.; cEOR célú polimerek előszelekciós módszere (Pre-selection method for cEOR polymers); *XXVIII. Nemzetközi Vegyészkonferencia* (Nagyvárad, Románia); 2022.10.27-29.

2. **Hartyányi, M.**, Nagy, R., Bartha, L., Puskás, S.; cEOR célú mozgékonyság szabályzó polimerek hidrodinamikai átmérőjének becslése dinamikai viszkozitás alapján; *II. FKF Szimpózium* (Online); 2021.06.16-18.

3. Puskás Sándor, Törő Mária, Vágó Árpád, Ördög Tibor, Tóth Marianna, Kálmán Gyula, Mátrai Andrea, Nagy Roland, Bartha László, **Hartyányi Máté**, Lakatos István, Szentes Gabriella, Dékány Imre, Janovák László, Geiger János; *Surfactant-Polymer Enhanced Oil Recovery Project at Algyő Field = Tenzides-Polimeres EOR Projekt Algyő mezőben*; *Országos Bányászati Konferencia* (Herceghalom); 2023.11.08-10.

4. Nagy, R., **Hartyányi, M.**, Bartha, L., Puskás, S.; Harmadlagos kőolajkitermelésben alkalmazható vízoldható polimerek vizsgálata gélkromatográfiás módszerrel; *XXIX. Nemzetközi Vegyészkonferencia* (Marosvásárhely, Románia); 2023.10.25-28.

9 Scientometric data

Number of publications forming the basis of the PhD thesis:	8
cumulative impact factor:	10,2
Number of publications related to the topic of the PhD thesis:	6
cumulative impact factor:	8,795
Total number of publications:	14
Total impact factors of publications:	18,995
Number of independent citations (based on Scopus):	8
H-index:	2

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