

10. AUTHOR'S REFERENCE of scientific contributions in all publications

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This summary of contributions is based on 36 peer reviewed (indexed in Scopus database) publications, including one book chapter, and 5 contributions in conference series. In Scopus, these papers have 1199 citations (excluding self-citations of all authors) with a corresponding Hirsch index of 17. These works are based on scientific research conducted mainly in the Institute of Physical Chemistry – Bulgarian Academy of Sciences (IPC-BAN), CanmetENERGY - Natural Resources Canada and the University of Alberta. The contributions can be grouped into the following research areas:

1. Mechanisms of stabilization of W/O petroleum emulsions and effect of different crude oil fractions.
2. Design of unique scientific instrumentation for studying thin liquid films.
3. Drainage kinetics and interactions in thin liquid films formed between a flat solid surface and approaching drop/bubble.
4. Impact of adsorption layer properties on thin liquid films behaviour.

All of these research areas are traditional for IPC-BAN. The main contributions in each area of scientific interest are summarized below, with references to the relevant publications following numbering in the document “List of all publications”.

1. Mechanisms of stabilization of W/O petroleum emulsions and effect of different crude oil fractions. [6, 10, 11, 12, 14, 15, 17, 18, 19, 20, 22, 23, 25, 26, 31, 33, 35]

During crude oil extraction, highly stable and undesirable water-in-oil emulsions are formed. The mechanism of stabilization of these emulsions is not fully understood yet. The application of microscopies scale studies of thin emulsion films to this problem led to a new understanding of underlying mechanisms and effects of different factors affecting emulsion stability.

1.1. Effect of bitumen concentrations and type of diluent (aromatic/aliphatic). [6, 11, 33, 35] Thin liquid emulsion films of bitumen solutions with different concentrations and solvent composition (mixtures of toluene (aromatic) and heptane (aliphatic)) were studied. The lifetimes,

thicknesses, and thinning rates of water-in-diluted bitumen films depend on solvent-to-bitumen ratio (S/B) and on the aromaticity of the solvent used. For aliphatic solvents, the emulsion film properties change abruptly at a well-defined dilution coinciding with the onset of asphaltene precipitation and previously observed critical S/B, at which bulk emulsion properties also change dramatically. Microscopic observations reveal that above critical S/B, water/oil interfaces become rigid and small asphaltene aggregates are formed. These results can provide guidance for optimizing froth treatment process.

1.2. A new mechanism for stabilization of W/O petroleum emulsions was proposed [6, 10, 11, 12]. Asphaltenes hierarchical aggregation can contribute to emulsion stability by forming a network structure within thin oil film, separating approaching water droplets. This structure changes the rheology of the film-forming oil to non-Newtonian with yield stress (gel-like), which can stop the film drainage before its critical thickness of rupture and thus stabilize the emulsions. The proposed stabilization mechanism does not invoke any surfactant-like amphiphilic nature of asphaltenes (which they don't possess despite claims in the scientific literature on the topic). The proposed new mechanism allowed an explanation of measured drainage kinetics of films, the obtained higher than expected equilibrium film thicknesses and non-draining dimples.

1.3. Revealing the role of different bitumen fractions in stabilization of W/O emulsions.[12] Drainage kinetics, thickness, and stability of water-in-oil thin liquid emulsion films obtained from asphaltenes, bitumen, and de-asphalted bitumen diluted in toluene were studied. The results showed that asphaltenes stabilize thin films at much lower concentrations than bitumen and de-asphalted fraction. The drainage of films containing asphaltenes is significantly slower than the drainage of the films obtained from bitumen and de-asphalted bitumen. The films stabilized by asphaltenes are much thicker (40–90 nm) than those stabilized by de-asphalted bitumen (~10 nm). Aging effects, including gradual increase of film thickness, rigidity of oil/water interface, and formation of submicrometer size aggregates, were observed only for films stabilized with asphaltenes.

1.4. Extracting and characterising asphaltene subfractions responsible for W/O emulsions stabilization. [15, 17, 19, 23, 25] Commonly, asphaltenes are divided in fractions based on their solubility in solvents with different degree of aliphatic content. We proposed a procedure for subfractionation of asphaltenes based on their interfacial activity. It was found that the most

interfacially active asphaltene (IAA) subfraction represents less than 2 wt % of whole asphaltenes (WA), but its removal had a profound effect on interfacial and film properties. It was found that the IAA subfraction adsorbed irreversibly at the oil–water interface and formed interfacial layers of low compressibility. IAA was characterised through comprehensive chemical analyses and the results were used to construct average molecular representations of IAA and remaining asphaltenes (RA) molecules. These structures were used in molecular dynamics (MD) simulation to study interfacial and aggregation behaviors of the proposed molecules. The MD simulation study showed that the IAA molecules self-assemble in solvent and form supramolecular structures and a porous network at the oil/water interface, as suggested in our previous work. In further refinements of subfractionation procedure we studied the effect of solvent aromaticity on extracted IAA and characterised their composition.

1.5. Effect of asphaltene aggregation on rheological properties of diluted bitumen. [18, 22, 31, 43] Viscosity of bitumen diluted in toluene, heptane and heptol (blend of heptane and toluene (80:20), by volume) solutions were studied for up to 30 days. It was found that above the critical dilution for onset of asphaltene precipitation, viscosity of the solutions decreases continually with aging, while in toluene and below the critical dilutions for heptane containing solvents, there was no detectable change in the viscosity. The decrease of the viscosity was related to the formation of asphaltene aggregates and aggregate clusters, which precipitated out and, as a result, decreased the bitumen (asphaltene) content of the solution. The observed time dependence of the viscosity reduction suggests that the asphaltene aggregation/precipitation is a continuous process with the time scale of weeks and is not limited to the relatively short period of initial massive precipitation. [18, 31] Capillary-driven flow of several pure liquids and bitumen diluted in heptol were studied using a nanofluidic chip. The filling kinetics was measured for each solution and compared to theoretical models. Theoretical model for capillary filling of Bingham Plastic fluid was developed to probe the possible non-Newtonian behavior of diluted bitumen above the onset of asphaltene precipitation. The results showed that Bingham Plastic model describes the rheological properties of bitumen solutions above the critical dilution (of 5 wt.% and 11 wt.% bitumen) more accurately than the Newtonian model and provide a better fit for capillary-driven flow at nanoscale. This study demonstrated that nanochannels are a promising experimental platform to analyze the flow of hydrocarbons in porous media. [22, 31, 43]

1.6. Demulsification mechanisms of water-in-crude oil emulsions. [14, 26] The modified version of the Scheludko-Exerowa cell [26] with a dosing system as described in section 2.3 was used to study the effect of demulsifiers to remove dispersed water from petroleum emulsions. The effect of biodegradable polymeric demulsifier (EC300) on heptol 5:5 (blend of heptane and toluene 50:50 by volume) dissolved asphaltene films were studied. We compared two ways of demulsifier addition: (1) EC300 was premixed in the oil phase before films formation; (2) stable films were formed from asphaltene solutions initially and demulsifier was dosed into the film. Addition of EC300 destabilized the initially stable film, which ruptured within 20 s after the addition. The experiments with the modified cell also revealed the overdosing effect of the demulsifier, forming more stable films at high EC300 concentration. A comparison of the experimental results between a dosed system and a premixed system confirmed the value of the modified cell to study the stabilization/destabilization processes of water-in-oil emulsions in a way that mimic more closely the real petroleum applications. In a complementary experiment with AR-G2 rheometer (TA instruments, USA) with a Double Wall Ring geometry, shear viscoelastic moduli of interface water/oil (2 g/L asphaltene-in-(5:5 heptol)) showed a build-up of strong elastic dominated interfacial layer which was reversed and gradually softened to fully “fluidlike” water/oil interface ($G' \rightarrow 0$ N/m) after addition of EC300. For the premixed asphaltene/EC300 system, negligible shear viscoelastic moduli were observed. Both types of experiments point that the destabilization mechanism is related to the disruption of the asphaltene network formed at the oil-water interface by EC300 demulsifiers.

A study of EO-PO based polymeric demulsifiers revealed that their addition soften the asphaltene film (i.e., reduce the viscoelastic moduli of asphaltene films) under both shear and compressional interfacial deformations. Study of the macrostructures and the chemical composition of asphaltene film at the toluene–water interface after demulsifier addition demonstrated gradual penetration of the demulsifier into the asphaltene film. Demulsifier penetration in the asphaltene film changed the asphaltene interfacial mobility and morphology, as probed with Brewster angle and atomic force microscopy. [14]

2. Design of unique scientific instrumentation for studying thin liquid [6, 16, 22, 26, 32]

2.1. Thin liquid film instrument for combined microinterferometric and electrochemical studies. As part of my postdoctoral visiting fellowship at CanmetENERGY, I build a novel and highly automated instrument that combined the traditional micro-interferometric thin liquid film (TLF) technique with electrochemical measurements of water-in-oil emulsion films. [6, 32]. This instrument allows for automated control of film formation, as well as for processing of experimental data on reflected monochromatic light, pressure, temperature using a custom-built LabVIEW program. The simultaneous and independent measurement of the thickness and size of the film by microinterferometric methodology and using electrical impedance studies of emulsion films provides novel opportunities for studying the structure and stability of oil films in an aqueous environment. [20, 32]

2.2. Integrated Thin Liquid Film Force Apparatus (ITLFFA). [16] A unique, fully custom-designed ITLFFA instrument was developed to simultaneously study dynamic force and spatial thin film thickness between deformable droplets/bubbles and solid surfaces. ITLFFA allows for measurements under a wide range of hydrodynamic conditions, with a displacement velocity of deformable surfaces ranging from 2 mm/s to 50 mm/s. Equipped with a high-speed camera, ITLFFA can provide information on interaction forces and thin liquid film drainage dynamics not only in a stable film but also in films of the quick rupture process (a few milliseconds). Because of its well-characterized experimental conditions, ITLFFA permits the accurate and quantitative comparison/validation between measured and calculated interaction forces and temporal film profiles. The new opportunities provided by this instrument were employed in our studies [16, 21, 24, 28] and followed by series of works by colleagues at the University of Alberta.

2.3. Modified Scheludko-Exerowa cell with dosing system. A new version of the Scheludko-Exerowa cell [26] was designed with a dosing mechanism which allows for addition of desired chemicals to the intervening organic liquid film that is already formed. While the thin liquid film (TLF) technique equipped with the original cell has proven to be a valuable tool for studying stability of dispersed systems such as emulsions and foams, many industrial applications involve the addition of various chemical aids to already formed dispersed systems with developed adsorption layers in order to modify the system and solve technical problems. Such applications

are not well represented with studies of premixed systems and will be more closely mimicked in the modified cell. The potential of the new cell was successfully demonstrated in studies with demulsifiers. [26]

3. Drainage kinetics and interactions in thin liquid films formed between a flat solid surface and approaching drop/bubble. [16, 21, 24, 28]

3.1. Effect of approach velocity on TLF drainage between and air bubble and flat solid surface. The dynamic drainage process of the liquid film trapped between an air bubble and a flat silica surface over a wide range of hydrodynamic conditions (Reynolds number from 0.005 to 135) is studied by a newly developed instrument integrated thin liquid film force apparatus (ITLFFA) under different salt concentrations. It was found that increasing the bubble approach velocity plays a significant role in the hydrodynamic pressure and fluid flow within the draining film promoting dimple formation and longer drainage time. The evolution of the draining film is analyzed using the Stokes–Reynolds–Young–Laplace (SRYL) model. Comparisons between theory and experiments indicate that the model captures the essential physical properties of the drainage system (e.g. the thickness of the first occurrence of the dimple as function of bubble approach velocity). [24]

3.2. Probing Boundary Conditions at Hydrophobic Solid–Water Interfaces by Dynamic Film Drainage Measurement. [2, 16] Using the newly developed ITLFFA, we reported a new approach for determining the degree of mobility of water on hydrophobic surfaces using the time-resolved evolution of thin-film profiles when a bubble interacts with a flat solid surface of variable surface hydrophobicities. For a given approach velocity of a bubble to a solid surfaces with increasing hydrophobicity in an electrolyte solution it was found that: (1) The dimple for the hydrophobic surfaces formed at much thinner film thickness than that for the hydrophilic case indicating decreased hydrodynamic pressure on the air bubbles; (2) The drainage rate of the liquid film increased with increasing surface hydrophobicity; (3) Unlike in the case of a hydrophilic surface where stable flat films were observed, rupturing films were observed in every experiments for hydrophobic silica surfaces; (4) Film rupture generally occurred at the barrier rim where the film thickness has minimum and expanded to the entire film within a few milliseconds. By comparing the measured film profiles with the predictions from the

Stokes–Reynolds–Young–Laplace model, the slippage boundary condition of water on the hydrophobic silica surface of surface nanoroughness was quantified.

4. Impact of adsorption layer properties on thin liquid films behaviour. [1, 2, 3, 4, 5, 7, 8, 9, 13, 29]

4.1. Impact of adsorption layer properties on drainage behavior of microscopic liquid films. [1-5, 8, 36, 37]. In a series of works, we've studied the relationship between equilibrium and dynamic adsorption properties of a single surface and thin foam film drainage kinetics and stability. It was demonstrated with different surfactant systems, including, anionic, non-ionic, cationic and their mixtures, that adsorption behaviour and dilatational rheology of surface layers are closely correlated with changes in drainage kinetics of thin foam film stability. Concentration regions where maximum of dilatational elasticity is observed are correlated with the transition from short living films to more stable ones. In the same concentration region, probability for observation of specific black patterns, black dots, and spots, increases significantly. These results are explained with the specific films hydrodynamics, mass transfer of surfactants from the bulk and in the surface layer that controls films tangential mobility and response to small instabilities.