CHAPTER I
INTRODUCTION

Due to an increase in global energy demand along with an insufficiency of conventional crude oils, it is of great importance for oil industries to develop their oil production techniques with the aim of optimizing an efficiency of crude oil extraction from a reservoir. However, there are many problems reducing capacity of crude oil production. One of the most common problems is the precipitation and deposition of asphaltenes in the pipeline (Mullins, 2007). Asphaltenes are constituent of crude oil defined as the components precipitating out of crude oil when mixed with n-alkanes, but soluble in aromatic solvents. It is believed that asphaltenes exist in crude oil as colloidal suspensions, which are stabilized by steric repulsion (Mullins *et al.*, 2012). They are the most polar, heaviest, polydispersed and have strong tendency for self-association (Haji-Akbari *et al.*, 2013). Variation in temperature, pressure and oil composition normally induced by the production and enhanced oil recovery could be the cause of destabilization of colloidal asphaltenes. The destabilized asphaltenes tend to aggregate into clusters and block pore spaces, plug tubing and foul downstream equipment, which causes a reduction in productivity and consequently results in significant remediation costs (Maqbool *et al.*, 2009). Therefore, it is extremely important to understand the factors that govern the asphaltene aggregation and precipitation.

In laboratory, the precipitation of asphaltenes is induced by adding precipitants directly into the crude oil or model oil. Upon precipitant addition, the insoluble part of asphaltenes will become unstable and aggregate kinetically. After a certain period of times, all of the insoluble asphaltenes will precipitate out of the solution and equilibrium solubility can be determined. Microscopy technique can be used to assess aggregation kinetics by measuring the onset time of precipitation. The equilibrium solubility can be measured by centrifugation technique. Both thermodynamics and kinetics of asphaltene precipitation are essential to investigate the asphaltene stability in crude oil (Maqbool *et al.*, 2009).

In 2013, Haji-Akbari *et al.* revealed the universality of asphaltene aggregation kinetics among different crude oils and solvents. They had established a unified aggregation model relating asphaltene stability with solution properties. They also investigated the effect of asphaltene concentration on aggregation kinetics over wide range of crude oils and asphaltene concentration. Basically, the aggregation rate of higher asphaltene concentrations is intuitively expected to be faster than the lower ones. However, upon a point,.the aggregation rate of high asphaltene content appears to be lower. According to the universal aggregation model observed beforehand, this counterinituitive effect is the result of competition between an increase in collision frequency, which increase with asphaltene concentration, and an increase in stabilization effect due to increase amounts of soluble asphaltenes (Haji-Akbari *et al.*, 2014). This hypothesis is solely based on numerical analysis of the aggregation model. More experimental evidences revealing the nature of soluble asphaltenes and their interaction in molecular level is needed, in order to verify the hypothesis.

Besides the other commonly known parameters governing asphaltene aggregation, the presence of dissolved molecular oxygen could be one of the overlooked parameters. It is commonly known that dissolved molecular oxygen can be the cause of polymerized hydrocarbon particles formation via autoxidation reaction (Taylor, 1974; Heneghan *et al.*, 1994; Erwin *et al.*, 1997). Since the oxygen can polymerized with hydrocarbons, it is reasonable to expect them to polymerized with asphaltenes and be the cause of asphaltene aggregation. Evidences from Electron Paramagnetic Resonance (EPR) studies and asphaltene precipitation under air and nitrogen atmosphere revealed the possible oxygen influences on asphaltene aggregation (Montarini *et al.*, 1998; Beck *et al.*, 2005). Quantification the influence of oxygen is crucial because most of researches are conducted under air atmosphere, which will be affected by the oxygen in air, including the aggregation model observed beforehand.

Therefore, the purpose of this study is to investigate the influence of soluble asphaltenes and dissolved molecular oxygen on the asphaltene aggregation in both kinetics and thermodynamics aspect. As a consequence, the universal asphaltene aggregation model will be validated for system containing these parameters.