CHAPTER I
INTRODUCTION

The precipitation and deposition of asphaltenes are undesirable situations which lead to many serious problems in oil production. In the reservoir, asphaltenes are considered to be soluble in the oil medium. Once oil production begins, changes that occur in composition, pressure and temperature may reduce the solubility of asphaltenes in the oil medium and can lead to precipitation and deposition of asphaltenes. Asphaltene deposition can cause well blockage, pipeline plugging and equipment fouling which have huge economic impact because of production losses and high remediation costs.

Asphaltenes are the heaviest and the most polar fraction of the crude oil that are soluble in aromatic solvents (i.e. benzene or toluene) but are insoluble in normal alkanes (i.e. *n*-pentane or *n*-heptane). Asphaltenes have a low H/C molar ratio of about 1.15 and also contain some heteroatoms (Speight, 1999). The asphaltene molecule has a diameter between 10-20 Angstroms and a molecular mass between 500-1000 Daltons (Groenzin and Mullins, 1999). Typically, asphaltene content in crude oils is determined by adding an excess amount of normal alkanes (40 times the crude oil volume) and then filtering the particles though a filter paper. Asphaltenes obtained in this manner are named based on the normal alkane used to precipitate them out (i.e. *n*-pentane asphaltenes or *n*-heptane asphaltenes).

The onset of asphaltene precipitation for a crude oil is usually determined by adding a normal alkane to the crude oil. Several methods have been utilized such as optical microscopy, spectroscopy, viscosity, electrical conductivity, and thermal conductivity (Donaggio *et al.*, 2001) to detect the precipitation onset point. Because the automatic titration system with UV-VIS spectroscopy is easy to operate and less time consuming than other methods, it has been used extensively to determine the asphaltene precipitation onset point at ambient condition. However, most crude oils are under high temperature and pressure conditions and commercially available automatic titration is not capable for such a high pressure. Therefore, the high pressure system with a high pressure cell (i.e. 15000 psi maximum pressure) and a laser near infrared (NIR) detector was constructed and was utilized to determine the asphaltene precipitation onset under high pressure conditions.

There are several thermodynamic models developed to predict the asphaltene precipitation onset point including solubility models, solid phase models, colloidal models and micellization models (Pina *et al.*, 2006). Also, several empirical methods exist which are capable of predicting the asphaltene precipitation onset. However, there is no experimental validation to these models.

In the case that asphaltene precipitation cannot be prevented, asphaltene dispersants are widely used to stabilize and stop asphaltenes from agglomeration into larger particles. Therefore, precipitated asphaltenes flow with the oil until they reach the separation facilities and can be properly removed.

In the first part of this work, thermodynamic solubility models and some empirical methods used to predict the asphaltene precipitation onset under live conditions were evaluated. A successful model was developed to predict the asphaltene precipitation onset under live conditions from the experimental data under ambient conditions. The model predictions were based on the experimental data under ambient conditions with the compositional data and crude oil properties from a tuned equation of state (EOS) database. The model prediction of the onset solubility parameter was validated using experimental data obtained from a high pressure experiment (high pressure titration and pressure depletion) with a laser near infrared (NIR) detector. Finally, asphaltene instability predictions of the live oil with miscible injectant (light hydrocarbons) were validated by pressure depletion experiment using a high pressure system.

In the second part of this work, measurement techniques were investigated and several proprietary blends of asphaltene dispersants were evaluated. Three experimental techniques have been utilized to evaluate and rank their effectiveness: automatic titration, particle size distribution, and turbidity measurement. By performing these experiments, the optimal amount of the optimal dispersant could be selected.