# CHAPTER II
LITERATURE REVIEW

2.1 n-Alkane Solubility

n-Alkanes are straight chained hydrocarbons with the general formula C_nH_{2n+2} (abbreviated C_n hereafter), where n represents the carbon number. When the temperature of an n-alkane solution drops below the n-alkane's solubility limit, known as the cloud point, the least soluble n-alkanes will precipitate out of solution as solid wax crystals (Paso et al., 2005). In the petroleum industry, cloud points are used to evaluate the wax precipitation potential of a fluid. Cloud points of n-alkane systems can be determined experimentally by several techniques. However, different techniques will yield different cloud points because they require different detectable wax crystal signals and do not represent true equilibrium (Hammami et al., 2003; Coutinho and Daridon 2005). Even when a small cooling rate of 0.01°C/min is used, large variations in the cloud point (3-4°C) can occur (Hammami et al., 2003). Cloud points can also be found by using thermodynamic models. In general, these models require the knowledge of various thermodynamic properties such as the enthalpy of fusion (ΔH_{fus}), the entropy of fusion (ΔS_{fus}) and interaction terms between the solvent(s) and solute(s) present in the systems (Uzomah, 2000). These models can predict the solubility of monodisperse n-alkane systems quite accurately, but are inaccurate for polydisperse n-alkanes systems in part because of the occurrence of cocrystallization (Beiny and Mullin 1987; Haulait-Pirson et al., 1987; Srivastava et al., 1997).

2.2 Cocrystallization

Cocrystallization is defined as a crystallization process where two or more species crystallize simultaneously and integrate into one crystal structure. If numerous species crystallize without cocrystallization occurring, the species are said to independently crystallize (Turner, 1971; Schwahn et al., 2002; Guo et al., 2004). In order for two organic species to cocrystallize, they must be similar in form and

dimension, and the pure components must have similar crystal symmetries (Turner, 1971). Cocrystallizing n-alkane systems will form a lamellar layer, where the larger n-alkane will bend to insert itself inside the layer and associate with a molecule with a smaller C_n as shown in Figure 2.1 (Singh *et al.*, 2000; Dirand *et al.*, 1998).
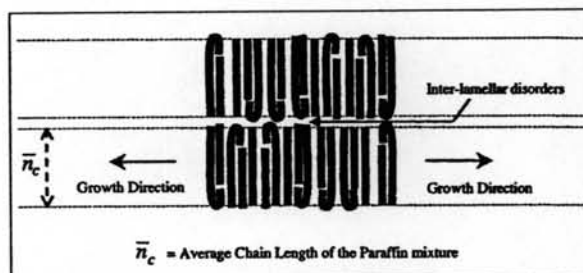
Figure 2.1 Lamellar structure of the multicomponent wax crystal (Singh *et al.*, 2000).

The degree of cocrystallization of binary n-alkanes is dictated by the degree of their miscibility. If two n-alkanes are totally miscible, then they can cocrystallize completely (Turner 1971; Guo *et al.*, 2004). Kravchenko has provided a rule to determine the miscibility of binary n-alkanes based on the difference in C_n between the materials as shown in Table 2.1 (Dirand *et al.*, 1998; Guo *et al.*, 2004).

Table 2.1 Kravchenko's rule where "Δn" represents the difference in carbon number between two n-alkanes (Note: there is an exception when $\Delta n = 1$ mainly due to the even/odd issue.)

	Miscibility		
Δn	Total	Partial	None
1	$n \geq 17$	$8 \leq n < 17$	$n \leq 7$
2	$n \geq 34$	$14 \leq n < 34$	$n \leq 13$
4	$n \geq 68$	$28 \leq n < 68$	$n \leq 27$

By using optical microscopy and differential scanning calorimetry (DSC), Guo *et al.* 2004 showed that C_{36}-C_{28}, C_{36}-C_{24}, C_{32}-C_{24}, and C_{32}-C_{24} systems in decane independently crystallize, and that C_{36}-C_{32} and C_{32}-C_{28} systems in decane cocrystallize, all consistent with Kravchenko's rule.

2.3 Polydisperse System

The yield stress of a wax gel is defined as the minimum stress needed to break the internal gel structure (Ashbaugh *et al.*, 2002a; Venkatesan *et al.*, 2005). In general, a lower yield stress is favorable because it limits wax deposition due to the shear provided from oil flow in pipeline will reduce the deposit (Guo *et al.*, 2004). The yield stress of polydisperse n-alkane gels growing in organic solutions are of interest because the yield stress of monodisperse n-alkane are decreased by a factor of 10 when another n-alkane is added, even though the amount of wax is doubled (Guo *et al.*, 2004). They also show that the yield stress for monodisperse systems generally increases when concentration increases, because more crystal networks are entangled inside the gel because of the n-alkane solubility limit (Venkatesan *et al.*, 2005; Beiny and Mullin 1987). Guo *et al.*, 2004 suggest that the gel yield stress of cocrystallized systems are higher than independently crystallized systems because cocrystallized systems form larger crystals and have less space in their gel network.

Other materials can also impact wax gel yield stress. For example, poly(ethylene-butene) (PEB) decreases the gel yield stress as concentration increases to a point. Once the PEB concentration reaches some critical concentration, an increase in PEB will actually lead to an increase in the yield stress as shown in Figure 2.2. When comparing the effect of PEB on gel yield stress for cocrystallized and monodisperse systems for the same wax content, it was found that cocrystallized systems are less affected by the presence of PEB (Guo *et al.*, 2004).
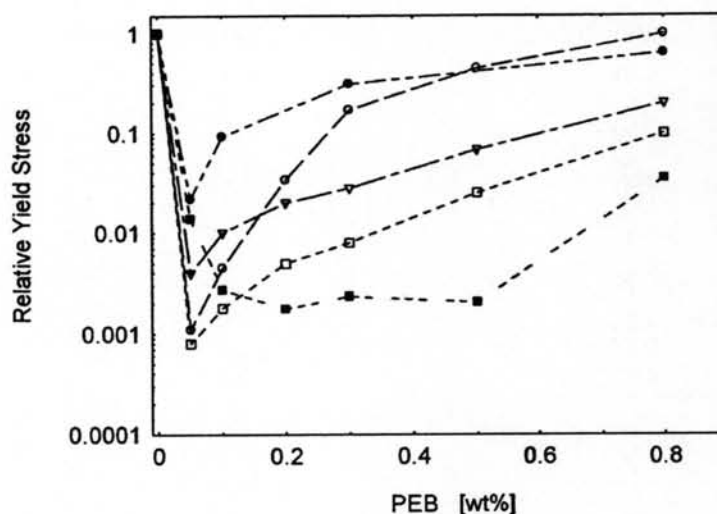
Figure 2.2 Effect of PEB on yield stress of paraffins and their mixture in decane at 0°C. (o) 4%C_{36}; (□) 4%C_{32}; (∇) 4%C_{28}; (●) 2%C_{36}-2%C_{32}; (■) 2%C_{36}-2% C_{28} (Guo *et al.*, 2004).

2.4 Gelation and Deposition Mechanism

The gelation of a wax-oil system occurs when growing n-alkane crystals interlock and form a volume-spanning crystal network or "house of cards" that traps oil in its interstitial spaces (Paso *et al.*, 2005; Ashbaugh *et al.*, 2002b). Gelation is the first step of wax deposition. When crude oil is sufficiently cooled, a fraction of hydrocarbons with carbon numbers above a certain value (the *critical carbon number*, CCN) precipitate out as stable crystals to form a gel with liquid oil trapped in the gel network (Singh *et al.*, 2000). Singh *et al.*, 2000 describe a wax deposition mechanism by the following steps:

1. Gelation of waxy oil at the cold surface (formation of incipient gel layer)
2. Diffusion of waxes (hydrocarbons with carbon numbers greater than the CCN) towards the gel layer from the bulk fluid.
3. Internal diffusion of these molecules through the trapped oil
4. Precipitation of these molecules in the deposit
5. Counterdiffusion of hydrocarbons with carbon numbers lower than the CCN out of the gel layer (aging).

This mechanism is confirmed by experimental results and other potential mechanisms, such as shear dispersion, Brownian diffusion, and gravity settling are not believed to be significant (Singh *et al.*, 2000; Jennings and Weispfennig, 2005). Wax will initially deposit very quickly, but the deposition rate will slow down and stop because the deposit acts as insulation, causing a decrease in the temperature gradient, a primary driving force for deposition.

2.5 Wax Deposition Experiment

Wax deposition can be simulated by either the use of a flow loop or a coldfinger apparatus, which basically consists of cold metal dipped into a vessel of hot oil (Paso *et al.*, 2003; Singh *et al.*, 2000). The coldfinger provides a simple and reliable method to simulate wax deposition, particularly for screening inhibitors. Using a coldfinger is preferable over a flowloop because it can be performed in short time periods and only small oil samples are required (Jennings and Weispfenning, 2005, 2006). One disadvantage of the coldfinger apparatus is that it has significantly different flow pattern than those present in production operations, thus not accurately simulating real piplines (Jennings and Weispfennig, 2005, 2006; Paso *et al.*, 2003). However, the coldfinger has proven to be sufficient for providing the CCN of an oil and investigating the impact of other materials on wax deposition (Jennings and Weispfennig, 2005, 2006; Paso *et al.*, 2003). The composition of wax deposits obtained from a coldfinger will vary with position. The deposit from the top part is the heaviest and contains the lowest wax fraction because it is exposed to less shear than the middle and bottom parts of the deposit (Jennings and Weispfennig, 2005). The change in deposit mass and composition with shear is consistent with Singh's work, which shows that when the flow rate of oil in flow loop increases, the wax fraction of the deposit increases and the deposit thickness decreases (Singh *et al.*, 2000). They calculated the temperature profile and found that the deposit ages faster at higher flow rates because the thermal boundary thickness at the oil-deposit interface decreases and the thermal gradient for deposition increases.