



CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Wax Precipitation

Wax or paraffin loses its solubility drastically when its temperature falls. At the temperature which an equilibrium solubility of wax is less than actual amount of wax in fluid, wax molecules start to precipitate as a crystal. The temperature that a first wax crystal formed and observed is called a cloud point temperature or wax appearance temperature (WAT). The wax appearance temperature is a thermodynamic quantity. It does not depend on operating conditions. Wax deposition, on the other hand, depends on the operating conditions such as flow rate and cooling rate.

Pure *n*-alkanes precipitate in various crystalline structures depending on a number of carbon atom (C_n) in a molecule (Dirand *et al.*, 2002),

Odd-numbered *n*-alkanes.

$13 < C_n < 41$: orthorhombic structure.

Even-numbered *n*-alkanes.

$14 < C_n < 26$: triclinic structure.

$28 < C_n < 36$: Monoclinic structure.

$C_n = 38, 40, 44, 46, 50$ and 60 : orthorhombic structure.

For multiparaffinic waxes, orthorhombic structures were observed in the precipitated solid. The distribution of *n*-alkanes also plays an important role in the precipitation of wax. Precipitated waxes form a single solid solution in a normal logarithmic distribution and form three different solid solutions in an exponentially decreasing distribution (Dirand *et al.*, 2002). Figure 2.1 shows the difference between both types of carbon number distribution.

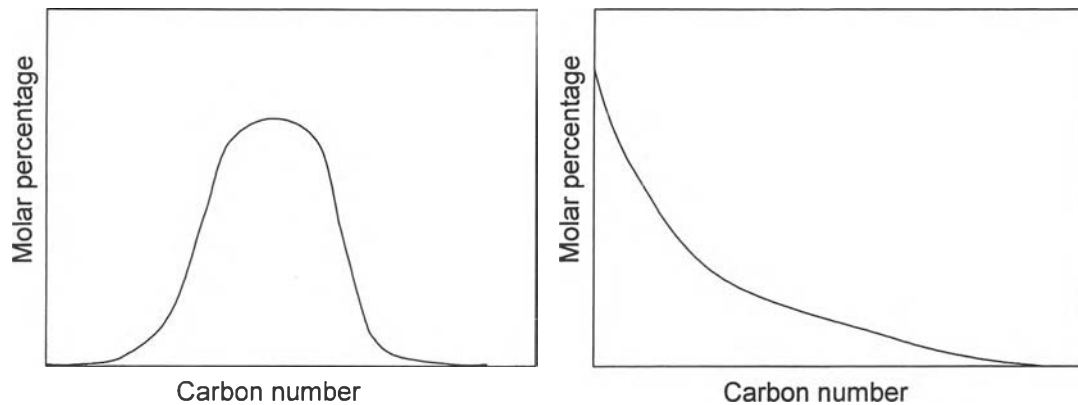


Figure 2.1 Carbon number distribution: (a) a normal logarithmic distribution, (b) an exponentially decreasing distribution (Dirand *et al.*, 2002).

2.2 Wax Deposition

When the crude oil is cooled to a certain temperature a fraction of heavy hydrocarbons precipitates out as stable crystals and forms a solid network which traps the remaining hydrocarbons inside. The formation of that network on the cold surface of pipeline is the first step of deposition process. The precipitation of paraffin out of the oil leads to a depletion of the dissolved paraffin concentration. Therefore, a gradient of dissolved paraffin concentration is established in the radial direction. This gradient leads to a mass flux of paraffin molecules towards the wall. The heavier molecules which have the carbon number greater than a critical carbon number, CCN, diffuse into the gel using trapped oil as a medium. In the same time, the light molecules, having carbon number lower than CCN, diffuse out to bulk liquid (Singh *et al.*, 2001). This phenomenon called aging leads to an increase of wax content in the wax-oil gel and also a deposit hardness with time.

2.3 Short-range Orientational Order

n-Alkanes are highly ordered in the solid state, existing in many crystalline structures which depend on the chain length. In the liquid state they still retain much of their order. The study of a molecular anisotropy using depolarized light scattering

by Bothorel (1968) has been shown that anti conformation (zig-zag or Z chain) having an optical polarizability in the direction of elongation superior to that of other directions. Hence, Z chains have a tendency to orient themselves parallel one to another. Figure 2.2 shows an example of anti conformation of *n*-butane.

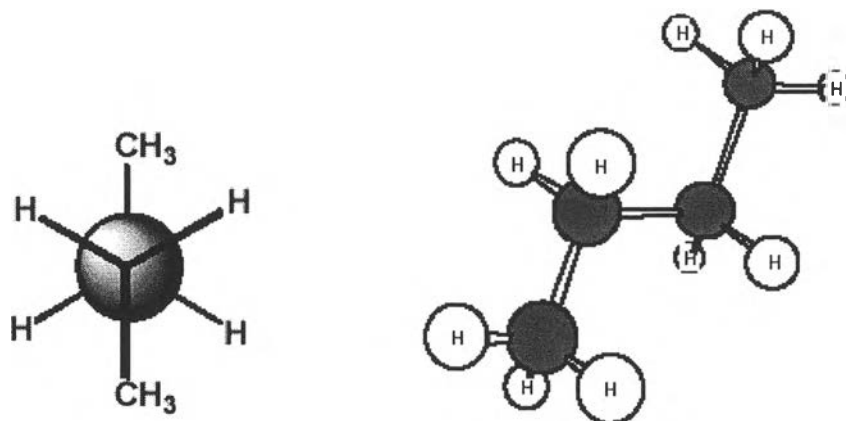


Figure 2.2 Anti conformation of butane.

The orientational order is highly sensitive to molecular shape. It increases with carbon number for pure *n*-alkane liquids and remains zero for the branched alkane. The existence of short-range orientational order is equivalent to an improved packing and would lead to negative contributions in the enthalpy and entropy of pure *n*-alkanes (Lam *et al.*, 1974). The net destruction of orientational order can be observed when *n*-alkane is mixed with solvent. Tancreade and coworker (1977) showed clearly that the spherical or globular solvent, such as CCl₄ and cyclohexane, destroys conformation order in liquid long-chain *n*-alkane, providing positive contribution of enthalpy and entropy of mixing. The net destruction of orientational order tends to increase with increasing sphericity of solvent, for example, net destruction of orientational order in hexacosane is the highest when solvent is cyclohexane and the lowest for *n*-hexane solvent. 2-Methylpentane destroys the order greater than *n*-hexane but less than cyclohexane. The molecular shapes of solvents are shown in Figure 2.3.

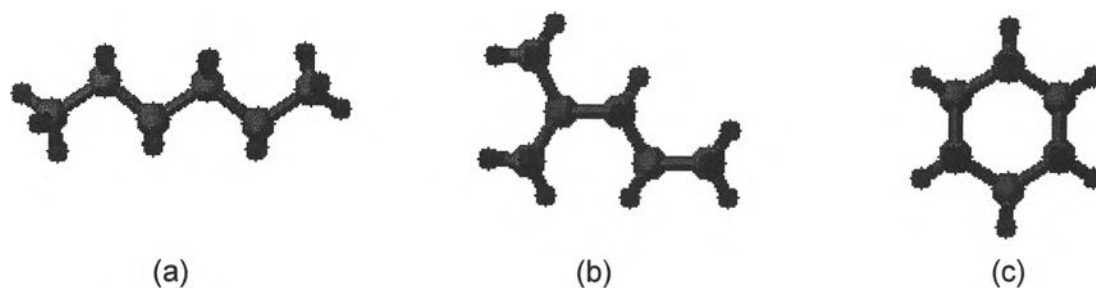


Figure 2.3 Molecular shape of solvents: (a) *n*-hexane, (b) 2-methylpentane, (c) cyclohexane.

2.4 Thermodynamic Models

Several thermodynamic models have been proposed to predict the precipitation of wax with different degrees of success (Won, 1986; Hansen *et al.*; 1988; Pedersen, 1995; Erickson *et al.*, 1993; Lira-Galeana *et al.*, 1996). Some models use the assumption of an ideal solid phase (Erickson *et al.*, 1993; Hansen *et al.*, 1989) or assume that precipitate as multiple pure solid phase (Lira-Galeana, 1996). Won (1986) used the regular solution theory of Scatchard-Hilderbrand in order to model the nonideality of liquid and solid phases, although his model had a tendency to overpredict cloud point temperatures. Coutinho (1996) proposed Wilson equations (Wilson, 1964) to describe the solid phase non-ideality. Liquid phase activity coefficients were calculated from the Flory free-volume model (Coutinho, 1995). Predictions of this model were superior to those of all other available models for multiparaffinic wax precipitation (Pauly *et al.*, 1998). The main deficiency of Wilson equations is the inability to predict multiple solid solutions occurring when the composition widens out. To overcome this problem, Coutinho (1999) proposed a model using the UNIQUAC equation instead of the Wilson equations to describe solid phase non-ideality. Dauphin and coworker (1999) showed that the model using UNIQUAC equation provided a better precipitation prediction than that using Wilson's equations.