



DETERMINATION OF WAX APPEARANCE TEMPERATURE (WAT) IN PARAFFIN/SOLVENT SYSTEMS BY PHOTOELECTRIC SIGNAL AND VISCOSIMETRY

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ABSTRACT

The wax appearance temperature (WAT) is the temperature at which the first wax crystals start to form, on cooling of paraffin/solvent systems. There are a number of different WAT determination methods, including: density and viscosity variation, differential scanning calorimetry, laser dispersion, and chromatography. The photoelectric method is used in this work based on the principle that the appearance of wax crystals modifies the transparency of the system. A comparison was made between WAT results obtained by photoelectric signals and viscosimetry. It was observed that the WAT results obtained by photoelectric signals are anticipated when compared with the viscosimetry data, demonstrating the enhanced sensitivity of the developed method.

KEYWORDS

paraffin; crystallization; WAT; photoelectric method; viscosity

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1. INTRODUCTION

In crude oils, paraffin deposition can occur by the growing of crystals directly onto the surface of pipelines or by crystal growth and agglomeration into the liquid environment, until reaching a critical volume and causing the reduction of the effective flow area of pipelines, which can ultimately lead to total blockage. The predominant deposition mechanism is dependent on the quantity and molecular weight of paraffin, the presence and type of emulsion and the conditions of temperature and shear imposed to the flow (Oliveira and Carvalho, 1998).

Paraffin precipitation increases the system apparent viscosity, promoting complete loss of fluidity, depending on oil composition and work temperature. For many years, the fluidity point had been used to foresee problems related with oil flow. It describes a physical property, corresponding to the lowest temperature at which the oil still flows under its own weight, when the rheological properties change drastically, starting to behave as a semisolid substance (Brüning, 1990). This change in the rheological behavior is associated with formation and growth of paraffin crystals in the medium (Oliveira et al. 2000).

The determination of the wax appearance temperature (WAT) is extremely useful to predict organic solid deposition at a given condition. Different methods can be used to determine the WAT of crude oil, such as cross polarization microscopy, viscosimetry, thermomicroscopy, fluidity point, and differential scanning calorimetry (DSC). These processes generally use specific and/or expensive equipments which makes difficult the WAT estimation in field works (Bello et al., 2005; Kok et al., 1996; Coto et al., 2008).

In the DSC method, the measurement of the heat released during solidification of paraffin crystals is the base to determine the cloud point. However, this technique can indicate WAT values which are lower than the real ones, mainly for crude oils with low paraffin content (Jiang et al., 2001).

In the optical microscopy method the measurement of the WAT is obtained by preheating and transferring a thin layer of the

sample to a microscopy slide to detect the appearance of paraffin crystals. This microscopy slide is connected to a controlled refrigeration system. The sample is viewed under polarized light so that only the crystallized material is visible, detecting more easily the beginning of the crystals appearance. When this method is used, the WAT is determined with reasonable exactness, however it is not a very practical method as a customary analytical tool.

In viscosimetry, the viscosity is determined at different temperatures. The cloud point of the crude oil is estimated by plotting viscosity values versus reciprocal temperature. Typically the cloud point is taken as the temperature where the data begin to deviate from linearity. As in DSC, this technique can provide values for WAT that are lower than the real ones (Campagnolo et al., 2000; Kadir and Ismail, 1997).

Taraneh et al. (2008) studied the inhibition of the crystallization and the melting point of Iranian raw oil samples using the rheological properties with the average scale of API gravity (American Petroleum Institute), and determined that the improvement of the flow depends on the molecular weight and the amount of asphaltene in the sample.

Lucas et al. (2004) studied a new additive which is able to reduce the pour point of oil samples. The method used to assess the cloud point of the samples was adapted from the ASTM Method D97/93 (1993) procedure, which consists in the determination of WAT when oil flow is not effected by gravity action only. Kané et al. (2004) evaluated the amount of crystalline materials as a function of temperature by using the DSC method. Additionally, steady viscosities were measured under various shear rates and at constant temperatures, aiming to understand the rheological behavior. Rheological modifications were attributed to changes in morphology of small paraffin crystallites in agreement with transmission electron microscopy observations.

Jiang et al. (2001) evaluated the benefits of the use of a temperature modulated differential scanning calorimetry (TMDSC). According to these authors, in a conventional DSC experiment the sample is subjected to a linear heating or cooling temperature rate, whereas in TMDSC a periodic

(usually sinusoidal) temperature modulation is superimposed on a constant underlying heating or cooling rate. They showed that the changes in the ADSC signals exhibit excellent correlations with WATs measured using conventional differential scanning calorimetry. **Elsharkawya *et al.* (2000)**, compared the values of WAT obtained by viscosimetry and DSC. They concluded that the viscosimetry method underestimates the WAT value.

Barbosa Júnior *et al.* (2007) proposed an experimental methodology to quantify and characterize the formation of paraffin in light hydrocarbons. They used the conductivimetry and thermometry techniques and concluded that both techniques can be used to determine solubility profiles of paraffin in light alkanes.

In this work a comparison on WAT values is made by carrying out photoelectric and viscosimetry techniques, using paraffin/solvent systems. The photoelectric signal uses a relatively simple methodology and enables the determination of the temperature at which the first wax crystals are formed (**Santana, 2005**).

2. MATERIALS AND METHODS

2.1 Materials

In the experimental procedure raw paraffin (RLAM 140/145-1) was used, dissolved in the following solvents: turpentine, diesel, n-paraffin, naphtha-petrochemical, hexane, and LCO (light cycle oil), all kindly supplied by RLAM (Landulpho Alves Refinery – PETROBRAS – Bahia – Brazil).

The standard cloud-point test method (D-2500-98) developed by **ASTM (1998)** is the most routinely used to determine the WAT temperature. According to this test, 40 mL of fuel are placed in a test jar that is cooled in an isothermal bath. The temperature of paraffin appearance is determined by direct visualization of crystals formed in the liquid phase. The temperature at which wax formation is initially observed is the cloud point.

2.2 Photoelectric Signal Method

The experiments to determine the WAT were accomplished using the following paraffin:solvent ratios: 1:99, 5:95, 10:90, 15:85, 20:80, 30:70, 40:60, 50:50, and 60:40 (wt.%).

To construct the WAT curves using the variation of photoelectric signals (PS), a DL50 Mettler Toledo Phototrode (error 0.5%) was used. The equipment has a spectrum that transforms the energy emitted into the experimental solution in a photoelectric signal which is modified according to changes occurring in the bulk solution, during sample cooling (wax crystal formation). The heating and cooling system (thermostatic bath) was connected to the phototrode, with the reactor agitation speed settled at 950 rpm during all experiments.

The photoelectric signal and temperature readings were acquired during sample cooling, from 60 to 5 °C (0.1 °C/min), until voltage stabilization. Before each experimental run, the equipment was calibrated with distilled water at room temperature (26 °C) to obtain 100% of light passing through the sensor. Using the experimental data, plots of the ratio of photoelectric signal and its maximal value (PS/PS_{max}) versus temperature (T) can be obtained. The maximal PS value corresponds to the readings at 60 °C, assuring that all paraffin present in the system is solubilized. The WAT value was determined as shown in Figure 1.

2.3 Rheological method

The rheological study was made using a Brookfield Rheometer (RS 2000), connected to a

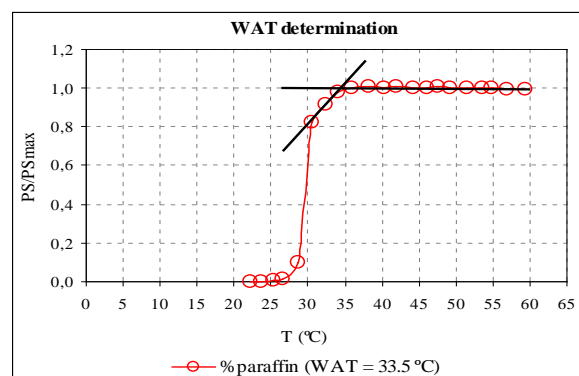


Figure 1. Determination of the WAT value by photoelectric signal method.

thermostatic bath. Readings of viscosity were taken at each decrease of 2 °C, from 60 to 15 °C, at a 0.1 °C/min cooling rate. In these experiments the temperature was not decreased until 5 °C, as in the photoelectric signal study, due to limitations of the equipment used to make readings at low temperatures and high viscosities. The paraffin concentrations evaluated were: 1, 5 and 10 wt.%. Values higher than 10 wt.% were not assessed due to the high viscosity. The deviation observed in the plots of viscosity versus temperature, caused by the precipitation of solid material, was used to define the WAT value (Giordani, 1993). The WAT value was determined as shown in Figure 2.

3. RESULTS AND DISCUSSION

3.1 WAT determination by using the photoelectric method

Figure 3(a-f) presents the plots of the ratio of photoelectric signal and its maximal value (PS/PSmax) versus temperature (T), from which the WAT values can be obtained. The determination of WAT is made in the nucleation stage, the first phase of paraffin crystallization, where the first crystals appear when the paraffin:solvent system is cooled (Figure 1).

By analyzing Figure 3(a-f), it can be observed that the photoelectric signal increases with increasing temperature. This behavior occurs because, above the temperature where the paraffin crystals appear, the environment shows transparency and the light pass through the

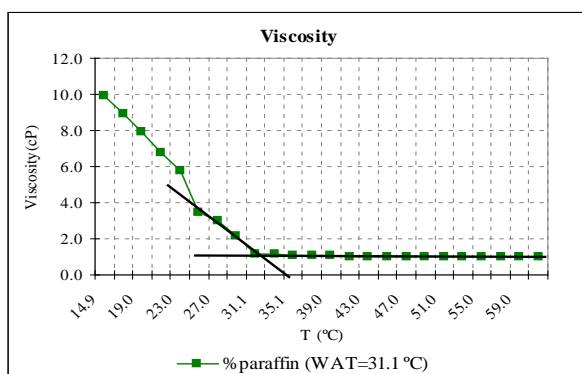


Figure 2. Determination of the WAT value by viscosimetry.

material. When the WAT value is reached, the system becomes biphasic (solid-liquid), showing a translucent or even cloudy aspect and the photoelectric signal decreases significantly. It was observed during the experimental procedure that the photoelectric signal intensity was greater for hexane, n-paraffin, naphtha-petrochemical, and turpentine solvents, when compared with diesel and the LCO ones. The dark color of the two last solvents affects the passage of the photoelectric signal, thus diminishing its intensity. However this fact does not modify the interpretation of the obtained data, because the equipment is calibrated for each solvent, according to the conditions to be evaluated, being the formation of wax crystals readily identified.

From Figure 3 (a-f) it can also be observed that, with increasing paraffin concentration, the variation of the photoelectric signal occurs at the highest temperatures, showing that the amount of paraffin present in the system has a direct influence on the temperature where the paraffin crystals start to form. This phenomenon can be explained by solid-liquid equilibrium phenomena, as described by Equation 1 (Won, 1986):

$$K_{SL} = \frac{s_i}{x_i} = \exp \left[\frac{\Delta H_f}{RT} \left(1 - \frac{T}{T_f} \right) + \frac{\Delta H_T}{RT} \left(1 - \frac{T}{T_T} \right) \right] \quad (1)$$

where:

K_{SL} - Solid-Liquid equilibrium constant, dimensionless;

s_i - mole fraction of component i (paraffin) in solid phase, dimensionless;

x_i - mole fraction of component i (paraffin) in liquid phase, dimensionless;

T - Equilibrium temperature - (WAT), K;

T_f - Fusion temperature of paraffin, K;

T_T - Temperature of phase transition, K;

ΔH_f - Enthalpy of fusion, cal·mole⁻¹;

ΔH_T - Enthalpy of phase's transition, cal·mole⁻¹.

For systems where the solid is solvent-free ($s_i = 1$), it can be observed that x_i is proportional to T , then the WAT temperature increases with increasing concentration of paraffin in the system.

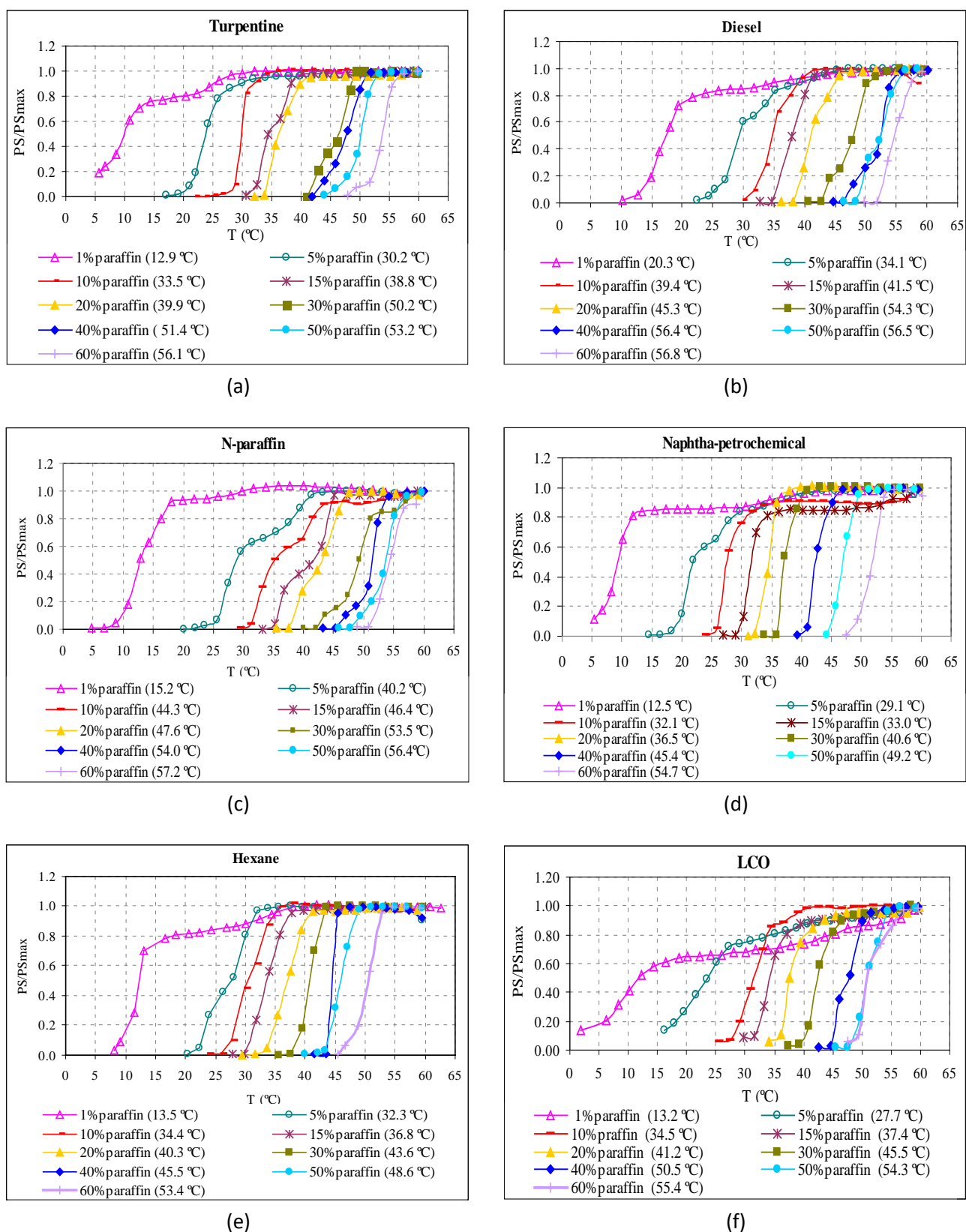


Figure 3. Determination of WAT by photoelectric signals for the used solvents: turpentine (a), diesel (b), n-paraffin (c), naphtha-petrochemical (d), hexane (e) and LCO (f), respectively. Values of WAT placed within brackets.

For all studied systems, hexane is the only solvent that is pure. All others are a mixture of many hydrocarbons in different proportions. When systems with 1 wt.% paraffin were cooled, the values obtained by photoelectric signal represents the crystallization of longer carbon chains, which reflects the turbidity temperature of the solvent itself. For hexane, the WAT value obtained is representative because the turbidity temperature is $-94\text{ }^{\circ}\text{C}$.

Figure 4 shows the WAT values obtained by photoelectric signal versus paraffin concentration (%) for each studied solvent. It can be observed that the lowest values for WAT were obtained with petrochemical naphtha and turpentine, probably due to the affinity and interaction of paraffin with the predominant linear hydrocarbon chains of these solvents. For hexane, due to its high vapor pressure and high volatility, the acquisition of the experimental data is rather difficult. The other studied solvents showed similar WAT values; however, due to the technical viability and easy availability, turpentine was recommended as a solvent for paraffin precipitation control in field applications.

3.2 Determination of WAT by viscosimetry

To determine the WAT values by viscosimetry, the same solvents were used. As explained in the experimental section, the paraffin concentration was varied in 1, 5 and 10 wt.%. Therefore, these

paraffin concentrations were used to compare the WAT values obtained by viscosimetry and photoelectric signal.

The plots of viscosity versus temperature for the paraffin/solvent systems are shown in Figure 5. The WAT values were graphically determined, corresponding to the inflection point of each curve.

Viscosity values were quantified through shear tension measurements ($0 - 4100\text{ s}^{-1}$ shear rate). In the cases where viscosity values were not proportional to the shear rate, more adequate models were applied to obtain the quantification of the viscosity. The models used in this research were the Ostwald de Waale (Power), the Bingham model or Ideal plastic, and the Herschell-Buckley model (Machado, 2002).

As observed for photoelectric signals, the WAT value increases with increasing paraffin concentration. Table 1 shows the WAT values obtained by viscosimetry and photoelectric signals. As can be noticed, the highest standard deviation values were obtained with low paraffin concentrations, indicating the greater sensitivity of the photoelectric signal method to determine WAT values.

It is important to point out that the WAT estimated by viscosimetry is identified only when the amount of wax crystals formed in the system is sufficient to modify viscosity, whereas by photoelectric signal it is identified as soon as the crystals are formed, thus justifying the variation in WAT values obtained by the evaluated methods.

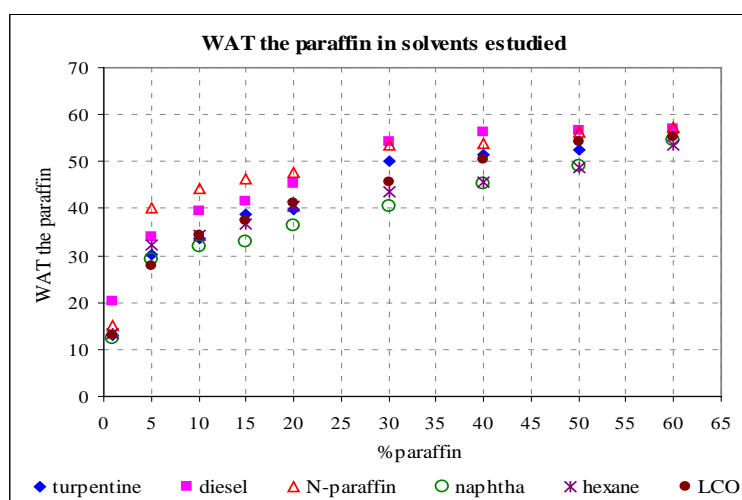


Figure 4. Curves of WAT of paraffin with the studied solvents obtained by photoelectric signal.

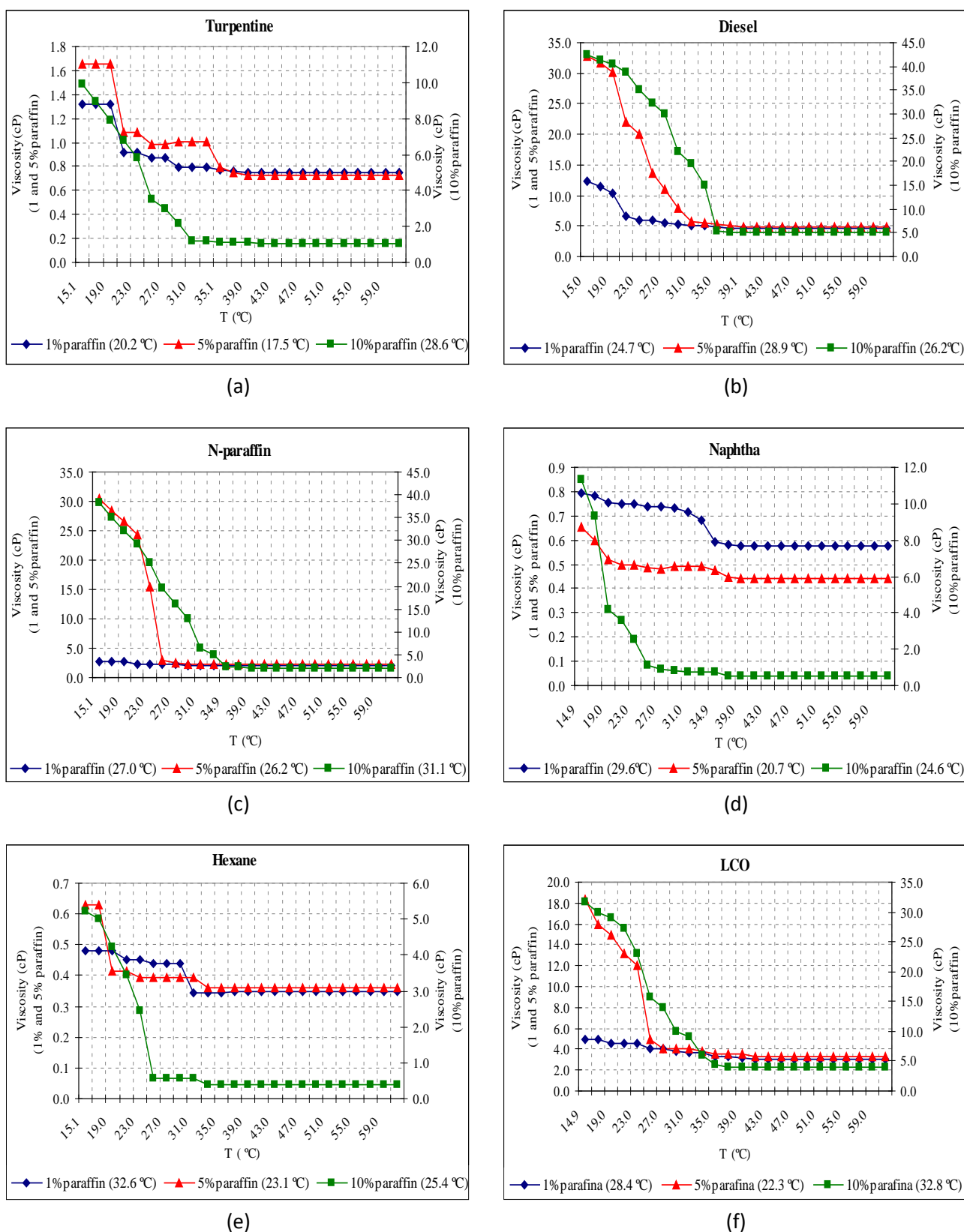


Figure 5. Plots of viscosity versus temperature for systems with 1, 5, and 10 wt.% paraffin in the following solvents: turpentine (a), diesel (b), n-paraffin (c), naphtha-petrochemical (d), hexane (e) and LCO (f), respectively.

Table 1. WAT of the studied systems by photoelectric signal (PS) and viscosimetry methods

% paraffin	WAT (°C) Turpentine			WAT (°C) Diesel			WAT (°C) n-paraffin		
	PS	Viscosity	SD	PS	Viscosity	SD	PS	Viscosity	SD
1	12.9	20.2	5.2	20.3	24.7	3.1	15.2	27.0	8.3
5	30.2	17.5	9.0	34.1	28.9	3.7	43.5	26.2	12.2
10	33.5	28.6	3.5	40.6	38.7	1.3	44.3	31.1	9.3
% paraffin	WAT (°C) Naphtha			WAT (°C) Hexane			WAT (°C) LCO		
	PS	Viscosity	SD	PS	Viscosity	SD	PS	Viscosity	SD
1	12.5	29.6	12.0	13.5	32.6	13.5	13.2	28.4	10.7
5	29.1	20.7	6.0	32.3	23.1	6.5	27.7	22.3	3.8
10	32.1	24.6	5.3	35.3	25.4	7.0	34.5	32.8	1.2

* Standard deviation

The determination of WAT by viscosimetry, when 1 wt.% paraffin was used, was not representative because the variation obtained in viscosity is very low, interfering directly in the interpretation of the data used to obtain WAT values.

4. CONCLUSIONS

The results presented in this paper indicate that the use of viscosimetry to determine WAT values has a very low sensibility, showing values that are lower than the real ones. In the case of the photoelectric signal method, the WAT values are higher because this method is able to identify the solid phase as soon as it is formed, better representing the solid-liquid equilibrium in solvent/paraffin systems.

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