PHASE CHANGES OF PETROLEUM MIXTURES BY MONITORING TEMPERATURE AND CONDUCTIVITY FOR PARAFFIN FORMATION

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Abstract. Along the petroleum transportation in pipelines and other stages of oil processing, paraffin generation is an important problem. In this work, an experimental methodology is proposed to quantify and characterize the paraffin formed in the crude oil. The thermometry technique was applied to determine the solubility profiles of the paraffin in different types of alkanes, all featuring short and linear chains. The conductivimetry technique was also used in the experiments as a filtering analytical method. An equilibrium cell and other required apparatus were projected and built to carry out the experiments. These devices permitted the simultaneous acquisition of temperature and conductivity data.

Keywords: wax; paraffin; thermometry; petroleum; oil; deposition; pipelines

1. INTRODUCTION

In the petroleum industry, wax deposition is a very important problem that may occur during several steps of the crude oil processing, such as extraction, storage and transportation in pipelines. This problem is mainly provoked by two groups of compounds present in the crude oil, namely paraffins and asphaltenes (Manning & Thompson, 1995). Paraffins, particularly, consist of linear hydrocarbons (C_{16} to C_{30}) and present melting points which are higher than the environment temperature. Paraffins are a whitish solid but may be obtained as a type of paste, depending on the conditions applied. Also, paraffins and asphaltenes can precipitate as solid particles. The deposition of these species is so relevant that can obstruct the pipelines and equipments, and, in extreme cases, stop the flow rate.

Variations in temperature and pressure of the crude oil can result in the vaporization of the light fractions and, when this fact is observed, the composition of the liquid phase is altered and may initiate the flocculation phenomenon. Although wax deposition is not the major factor that promotes the interruption of the flow rate, it generally causes many operational problems.

Two factors can cause wax deposition: (a) reduction of the temperature of the oil down to the level where the paraffin precipitates and (b) separation of asphaltenes from the crude oil, causing the formation of solid deposits (Carnahan, 1989). Asphaltenes may be found either in the form of agglomerated particles or in suspension in the crude oil, effected by the presence of resins. If for some reason the resins are removed, the asphaltenes flocculate, aggregate and finally form solid deposits (Tawer & Dick, 1990). Light hydrocarbons would facilitate by keeping the precipitation point at a higher value, thus increasing the solubility of the paraffin compounds in the crude oil.

Along the productive life of an oil well, the process of extraction tends to become more difficult. Light fractions, which solubilize heavy fractions, are removed first, and the residual fractions increase the viscosity of the fluid. The formation of solid materials can be observed. In these circumstances, the knowledge of phase equilibrium data is very important.

Each type of solid materials produces different types of obstructions in the pipelines, as well as in the porous medium in the reservoir tanks. Thermodynamic models are indispensable tools in that they are capable of predicting in which conditions wax deposition can occur. These models are formulated with basic data of the compounds contained in the oil and their properties in the mixture.

The thermometry technique has been applied in the determination of salt solubility (Tavares et al., 1999). This method is based on the thermal variations observed during the time of experiment. The temperature of the system affects the enthalpy of the existent phases or of those that appear or disappear in the medium. Therefore, in this methodology, an initial mixture of known composition was monitored as a function of time and temperature.

In view of this, the main motivation for the present work was to provide helpful information to the petroleum industry with regards to the quantification and characterization of the formation of paraffins, by using a simple and efficient methodology. Furthermore, novel experimental data for the scientific literature on solid-liquid equilibrium of hydrocarbons are presented in this work.

2. MATERIALS AND METHODS

2.1 Materials

The following reagents were used in the experiments: n-pentane (C_5H_{12}, 99%), n-hexane (C_6H_{14}, 95%), n-heptane (C_7H_{16}, > 99%), n-decane ($C_{10}H_{22}$, > 95%), n-dodecane ($C_{12}H_{26}$, >99%) and commercial paraffin (melting point 55-56°C). All these chemical products were supplied from Merck, except the commercial paraffin (Qteel). Crude oil samples were collected from fields in the States of Rio Grande do Norte and Bahia (Brazil).

2.2 Apparatus

Two different systems were used in the monitoring of the experimental measurements. The first system is the AqDados® acquisition software, which comprises an analogical-digital-analogical (AD/DA) converter, a digital thermometer (RTD PT100) coupled to a microcomputer, an equilibrium cell, a magnetic stirrer (Fisatom®, 752A) and a thermostatic bath (Heto®, 03 DBT 623). This system is represented in Figure 1. This apparatus is normally used in solid-liquid equilibrium experiments based on Quasi-Isothermal Thermometry (Tavares et al., 1999).

The second system was built with the purpose of simultaneously determining temperature and conductivity data. This apparatus consisted of a conductivimeter

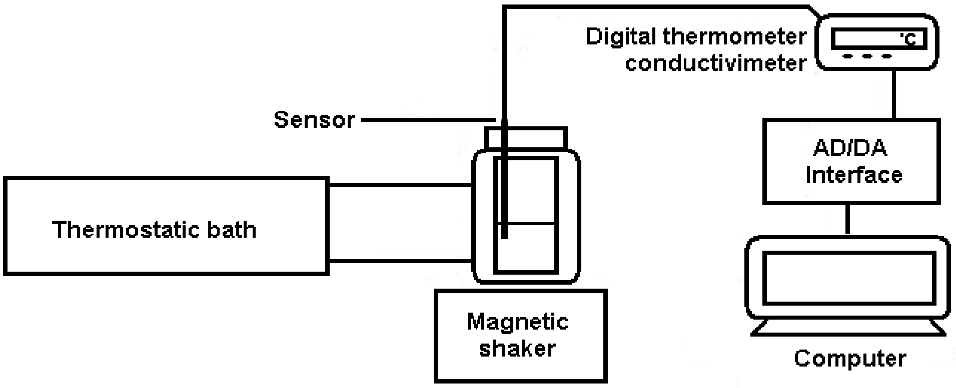


Figure 1. Schematic of the apparatus used in data acquisition during solubility measurements.

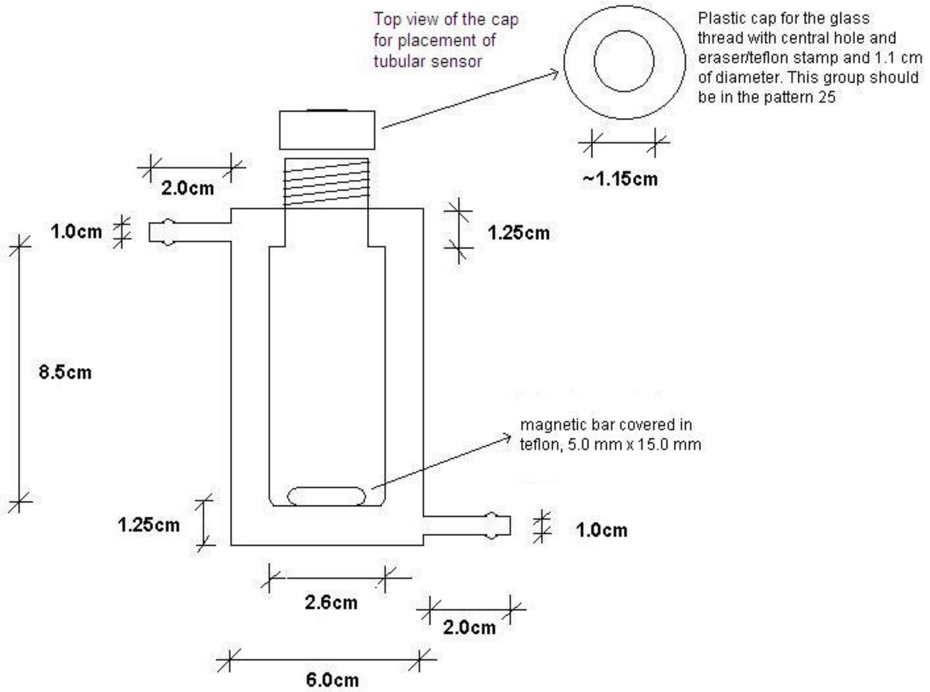


Figure 2. Design of the equilibrium cell for solubility measurements.

(Digimed®, DM-31), a conductivity cell made in stainless steel (Digimed®, DMC 100M, k=10 cm^{-1}), a magnetic stirrer (Tecnal®, TE-081), a thermostatic bath (Tecnal®, TE-1842) and an equilibrium cell (liquid volume of 45 mL), specially designed for these experiments. This cell is shown in Figure 2.

2.3 Experimental procedure

The equilibrium cell is filled up with a sample presenting a gravimetrically known composition of paraffin in the organic solvent (a light alkane). This system is allowed to stir and constant temperature until complete fusion and homogeneity. The thermostatic bath is programmed so as to gradually decrease the temperature of the system until a temperature below the melting point of the paraffin. Parameters like experimental time, temperature and conductivity are continuously recorded at a data computational system, from the point when cooling started.

3. RESULTS AND DISCUSSIONS

In this section, the experimental results are presented. The binary paraffin sytems studied comprised a series of linear alkanes, i.e. hexane, heptane, decane and dodecane.

3.1 Thermometry Experiments

Using the methodology and the apparatus presented previously, it was possible to generate the solubility profiles of the following systems: pentane (C_5) + paraffin, hexane (C_6) + paraffin, heptane (C_7) + paraffin, decane (C_{10}) + paraffin and dodecane (C_{12}) + paraffin. The points corresponding to the formation of paraffin as solid particles can be observed in plots of temperature versus cooling time of the equilibrium cell. Mathematical differential analysis was used to improve the accuracy in the determination of these points where the cooling rates suffer stronger alterations. Some illustrative experimental profiles, obtained in this work, can be shown in Figure 3.

3.2 Solubility Profiles

The experimental data obtained have been used to generate the solubility profiles of paraffins in light hydrocarbons systems. It was assumed that the paraffins were constituted by hexacosane (C_{26}) based on the solidification temperature and on the model of Won (1986), which considers the molar mass of the paraffin. The criterion of isofugacities was applied between the solid and the liquid phases, where the solid phase is considered as being a pure substance (Pan & Radosz, 1999). Equation 1

$$\ln\left(\frac{f^{L}_{i,puro}}{f^{S}_{i,puro}}\right) = \frac{\Delta H_m}{RT_m}\left(\frac{T_m}{T} - 1\right) + \frac{\Delta C_P}{R}\left(1 - \frac{T_m}{T}\right) - \frac{\Delta C_P}{R}\ln\frac{T}{T_m} + \frac{\Delta v}{RT}\left(P - P^{sat}_i\right) \tag{1}$$

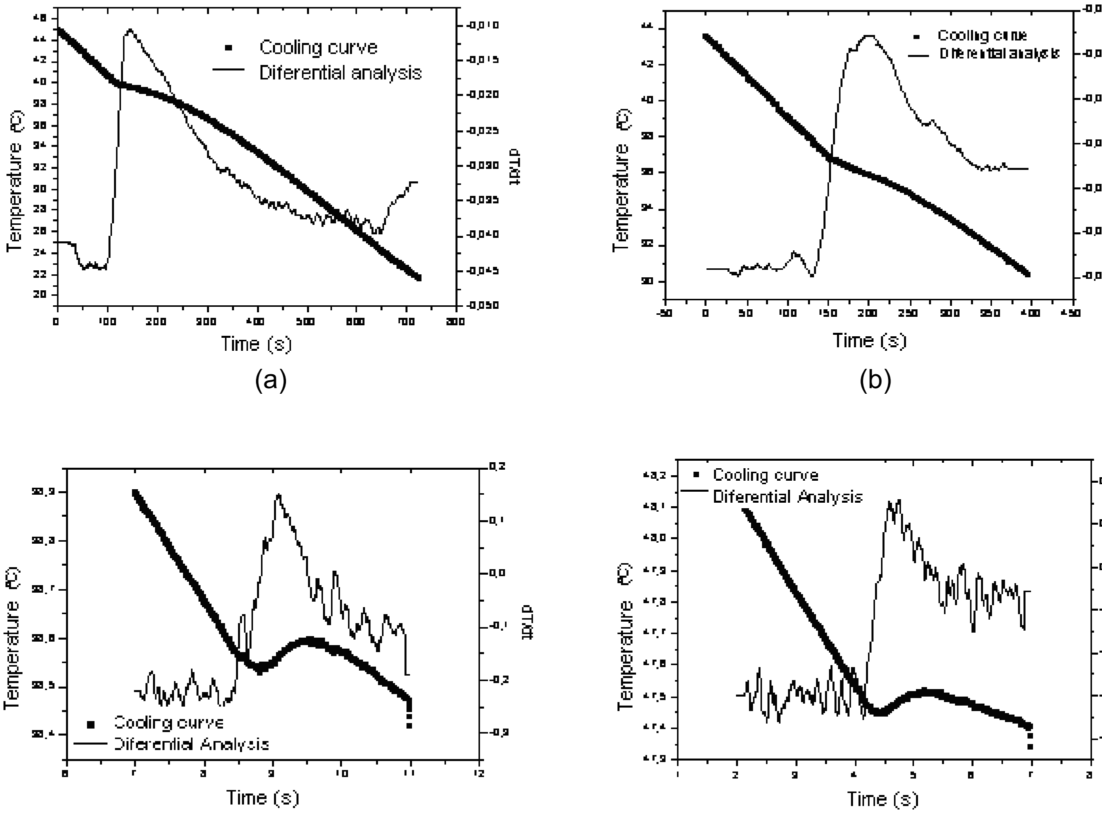
Where: $\Delta C_P = C^L_P - C^S_P$ and $\Delta v = v^L - v^S$.

was obtained from the relations between the fugacities of the solid and liquid phases using a thermodynamic cycle (Pan & Radosz, 1999; Prausnitz et al., 1986).

The experimental results are numerically listed in Tables 1 through 5 and depicted in Figures 4 through 8. A comparison between the ideal solution model, using the thermochemical properties, and the experimental results has been carried out. Particularly with respect to the paraffin-in-heptane system, the experimental data were compared with results presented in a previous work by Provost et al. (1998).

When compared to the ideal model, the experimental data obtained by Provost et al. (1998) presented deviations of 6.25% and 14.01% with regards to the mass percentage and molar fraction measurements, respectively (Figure 8).

In the case of systems constituted by light hydrocarbons, the ideal model represents the solubility profiles satisfactorily. This fact can be observed in Figures 4 through 8. It has been demonstrated that the method proposed for the determination of the solubility of the paraffins in hydrocarbons demonstrates is adequate. Furthermore, it could be observed that the profile generated from the experimental data,



(a) (b)

(c) (d)

Figure 3. Profiles of the cooling and mathematical differential analysis for different systems containing paraffin for the determination of the temperature of formation of paraffin as solid particles: (a) 40% in mass of paraffin in heptane, T = 40.8ºC; (b) 50.2% in mass of paraffin in pentane, T = 37.9ºC; (c) 34.3% in mass of paraffin in heptane, T = 43.4ºC; and (d) 30.2% in mass of paraffin in decane, T = 47,5ºC.

Table 1. Experimental data from the solubility profiles to the $C_5 + C_{26}$ system.

T (ºC)	%wC_{26}	xC_{26}	%wC_{26} calculated	xC_{26} calculated	Deviation (%) wC_{26}	Deviation (%) xC_{26}
56.0	100	1	100	1	0	0
40.8	60	0.228	66.51	0.281	9.78	18.88
37.9	49.75	0.163	58.51	0.217	14.97	24.93
32.7	35.12	0.096	44.29	0.135	20.70	28.83
30.6	27.13	0.068	38.87	0.111	30.20	38.61
27.3	20	0.047	31.02	0.081	35.52	42.32
24.6	15.11	0.034	25.33	0.063	40.35	45.93
18.0	9.95	0.021	14.52	0.032	31.49	34.23
-129.7*	0	0	0	0	0	0
			Average deviation (%)		20.33	25.97

*Data from literature (Daubert and Danner, 1995).

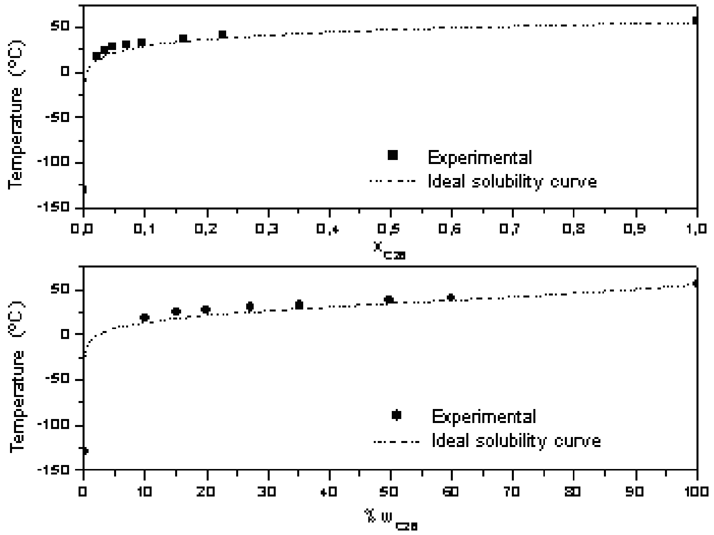


Figure 4. Solubility profile to the system $C_5 + C_{26}$ from the thermometry experiments.

Table 2. Experimental data from the solubility profiles for the $C_6 + C_{26}$ system.

T / ºC	%wC_{26}	xC_{26}	%wC_{26} calculated	xC_{26} calculated	Deviation (%) wC_{26}	Deviation (%) xC_{26}
56.0	100	1	100	1	0	0
38.0	49.94	0.190	54.42	0.219	8.24	13.33
34.7	40.00	0.135	45.24	0.163	11.58	16.69
32.1	29.60	0.090	38.43	0.128	22.98	29.70
30.2	24.55	0.071	33.79	0.107	27.34	33.66
26.3	19.94	0.055	25.32	0.074	21.26	25.09
23.3	14.97	0.040	19.87	0.055	24.67	27.86
18.6	9.90	0.025	13.16	0.034	24.78	26.81
9.5	5.04	0.012	5.39	0,013	6.53	6.80
-95.3*	0	0	0.00	0	0	0
			Average Deviation (%)		14.74	17.99

*Data from literature (Daubert and Danner, 1995).

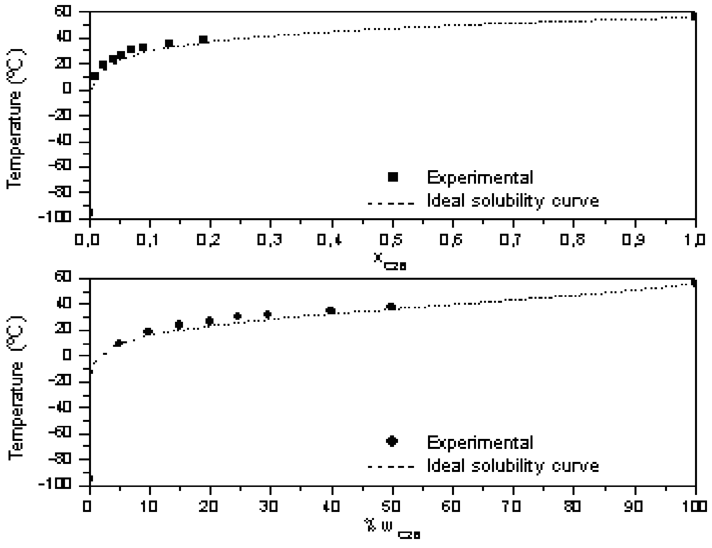


Figure 5. Solubility profile to the system C_6 + C_{26} from the thermometry experiments.

Table 3. Experimental data from the solubility profiles for the C_{10} + C_{26} system.

T / ºC	%wC_{26}	xC_{26}	%wC_{26} calculated	xC_{26} calculated	Deviation (%) wC_{26}	Deviation (%) xC_{26}
56.0	100	1	100	1	0	0
47.5	69.80	0.473	72.05	0.500	3.13	5.46
43.2	54.78	0.320	57.73	0.346	5.11	7.68
37.4	35.86	0.178	40.31	0.208	11.05	14.16
33.6	24.98	0.114	30.75	0.147	18.76	22.15
31.5	20.61	0.092	26.18	0.121	21.28	24.35
25.4	10.31	0.043	15.75	0.068	34.56	36.88
19.8	5.19	0.021	9.43	0.039	44.98	46.45
-29.7*	0	0	0	0	0	0
			Average Deviation (%)		15.43	17.46

*Data from literature (Daubert and Danner, 1995).

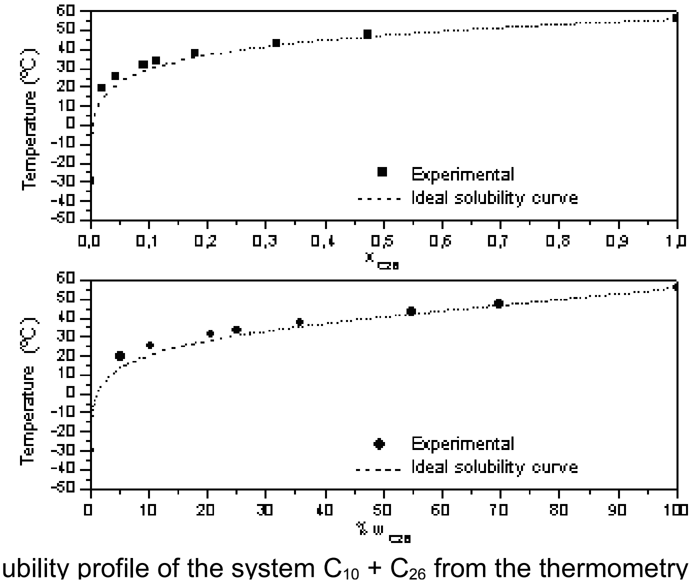


Figure 6. Solubility profile of the system C_{10} + C_{26} from the thermometry experiments.

Table 4. Experimental data from the solubility profiles for the C_{12} + C_{26} system.

T / ºC	%wC_{26}	xC_{26}	%wC_{26} calculated	xC_{26} calculated	Deviation (%) wC_{26}	Deviation (%) xC_{26}
56.0	100	1	100	1	0	0
41.8	44.95	0.275	48.77	0.307	7.84	10.33
37.0	29.93	0.166	35.03	0.200	14.57	17.35
32.9	20.01	0.104	25.59	0.138	21.82	24.44
26.7	10.02	0.049	15.17	0.077	33.97	35.89
21.1	5.01	0.024	9.07	0.044	44.74	45.97
-9.6*	0	0	0.00	0.000	0.00	0.00
			Average Deviation (%)		17.56	19.14

*Data from literature (Daubert and Danner, 1995).

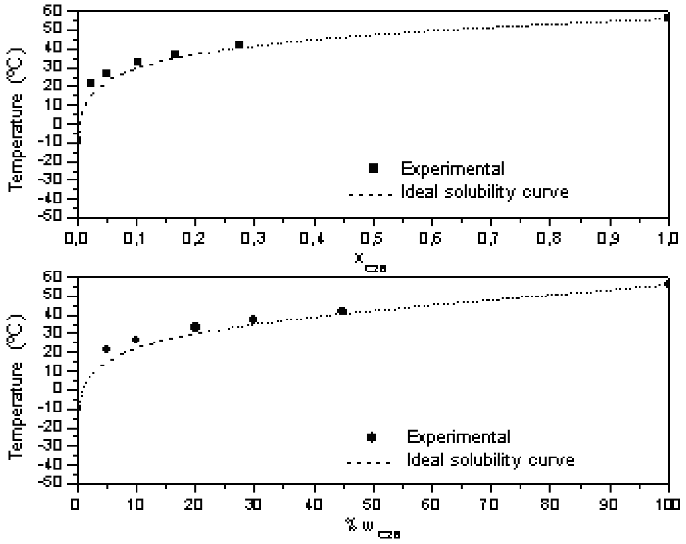


Figure 7. Solubility profile of the system C_{12} + C_{26} from the thermometry experiments.

Table 5. Experimental data from the solubility profiles for the C_7 + C_{26} system.

T / ºC	%wC_{26}	xC_{26}	%wC_{26} calculated	xC_{26} calculated	Deviation (%) wC_{26}	Deviation (%) xC_{26}
56.0	100	1	100	1	0	0
43.4	65.69	0.343	66.57	0.352	1.32	2.53
38.5	51.58	0.225	52.10	0.229	1.01	1.61
32.6	34.78	0.127	36.15	0.134	3.80	5.08
27.5	23.09	0.076	24.85	0.083	7.07	8.49
22.2	10.42	0.031	15.98	0.049	34.78	37.63
-90.6*	0	0	0	0	0	0
			Average deviation (%)		6.85	7.91

*Data from literature (Daubert and Danner, 1995).

obtained in this work, presents a behavior which is similar to that of the ideal model, as expected. The proposed method is relatively simple and the experimental data were consistent with those provided both by the ideal model and the experimental data from previous works (Provost et al., 1998). Non-idealities of the liquid phase could also be taken into account through an activity coefficient factor or model. However, these results demonstrated that it is not so relevant depending on the accuracy, which is the case for the real mixtures.

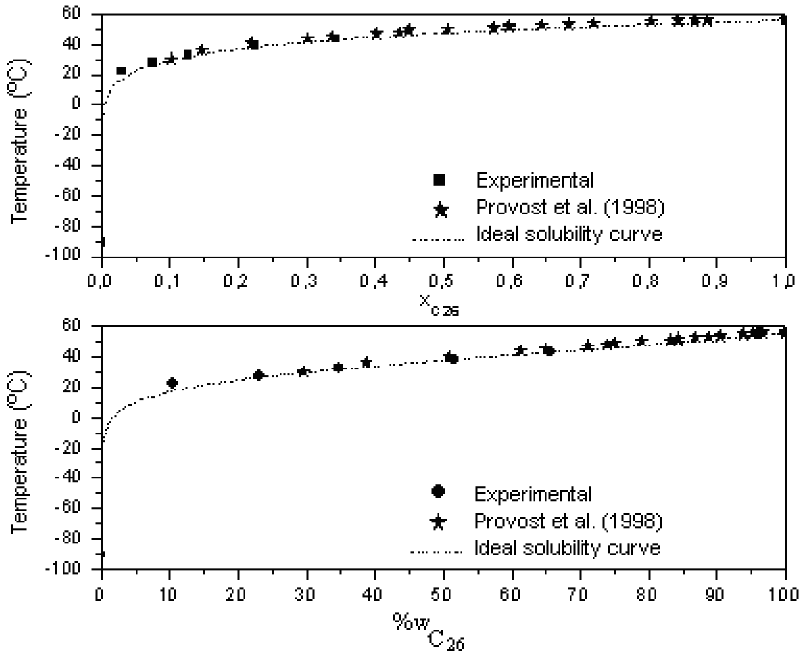


Figure 8. Solubility profile of the system C_7 + C_{26} from the thermometry experiments.

3.3 Real Mixtures

The experimental methodology used in this work was also used for the identification of phase changes in real mixtures of hydrocarbons represented by samples of petroleum from oil fields from two different regions in Brazil (the States of Bahia and Rio Grande do Norte). The crude oil from Bahia used in this work is predominantly paraffinic and the oil from Rio Grande do Norte is classified as naphthenic. Three experiments were carried out following the same methodology in order to analyze and interpret the results obtained. It was also possible to detect alterations in the phases, during the fusion and the solidification phenomena alike. Figures 9 through 11 show the experimental heating and cooling curves obtained.

The results relative to the crude oil confirmed the characteristics of the crude oil

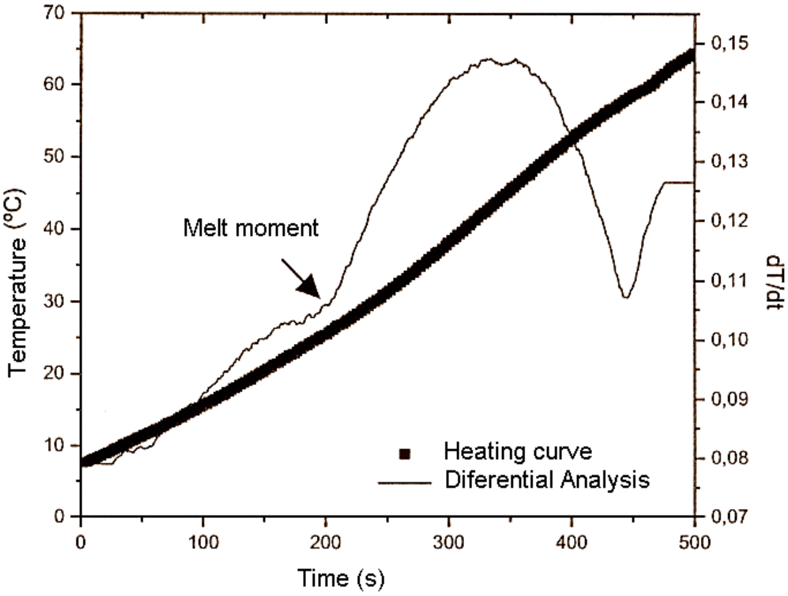


Figure 9. Measurements for the determination of the melting point of the crude oil from Rio Grande do Norte oil field, T = 26.1°C.

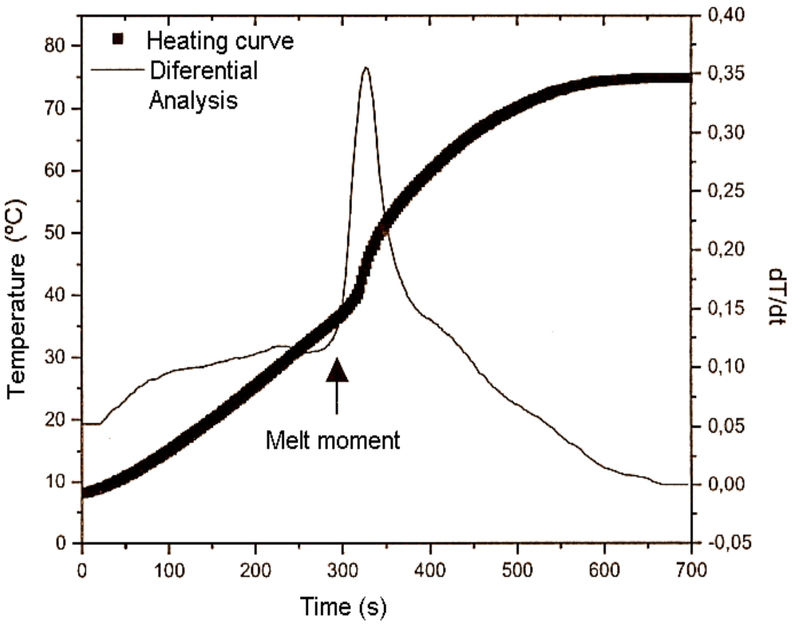


Figure 10. Measurements for the determination of the melting point of the crude oil from Bahia oil field, T = 36.5°C.

from the Bahia and Rio Grande do Norte oil fields. The former features a significantly higher concentration of paraffins than the latter, in that the melting point is a crescent function with regards to the paraffin content. The determination of the melting point for these two types of petroleum permits the prevention of problems caused by undesired phase changes during the different processes in the petroleum industry. Furthermore, this method can be applied in the determination of the concentration of paraffins in the crude oil.

3.4 Conductivity Measurements

The determination of the solubility was also carried out by the conductivity technique during the cooling of the crude oil samples. The objective was to determine the solidification or the fusion point. A special sensor was used for low conductivities (Digimed®).

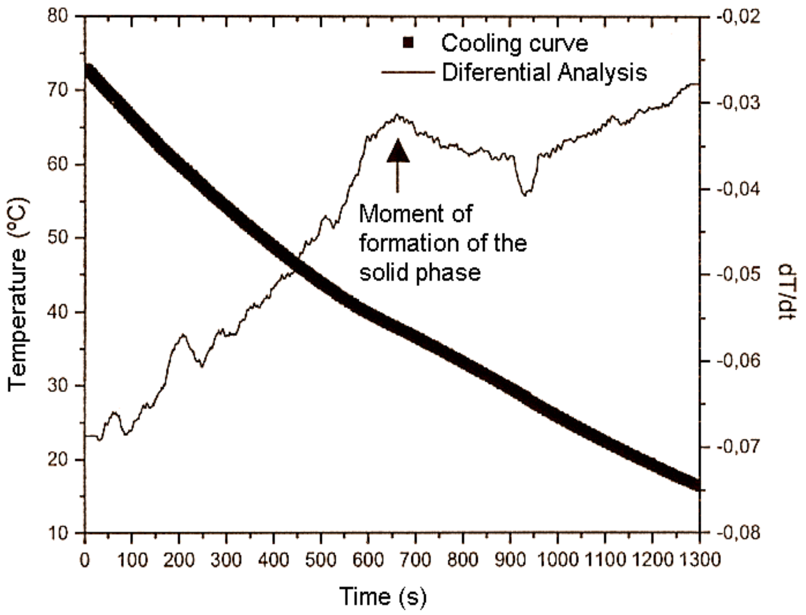


Figure 11. Measurements for the determination of the solidification point of the crude oil from Bahia oil field, T = 38.0°C.

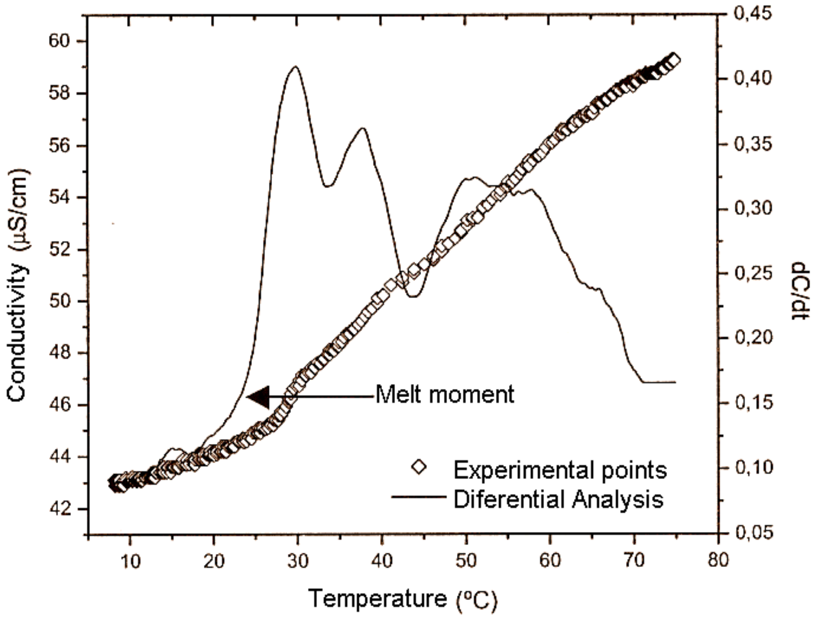


Figure 12. Measurements of conductivity (heating curve) for the determination of the melting point of the crude oil from Bahia oil field, T = 26.3°C.

The conductivity of a solution is a function of temperature and mobility of the molecules. Alkanes present low conductivities, which is justified by the fact that alterations in this specific property were intrinsically related to the mobility of the molecules in solution and to changes caused by the increase in temperature provoked by the heat released in the formation of the solid phase. The utilization of this technique was satisfactory in identifying the solid particles formation, at concentrations up to 50% in paraffins.

The mathematical interpretation was very similar to that suggested in the thermometry experiments. It could be observed that changes occurred in the profile of the conductivity as a function of temperature, which was caused by the formation of solid phases in the solution. Figure 12 shows experiments carried out using samples of petroleum from the Bahia oil field. The experimental results indicate the feasibility of the conductivity for the determination of the melting point of paraffins in solutions of light alkanes or in crude oil.

Table 6 presents comparative results between the temperatures obtained in the thermometry and the conductivimetry techniques. The results also demonstrate that the conductivimetry technique can be used to determine the solidification or melting point of paraffins in light alkanes or in crude oil. It must be pointed out that, for the crude oil, the conductimetric technique presented a lower melting point, indicating a more sensitive characteristic for detection.

Table 6. Comparison between the temperatures when an alteration in the phase is observed in five different samples (by thermometry and conductivimetry techniques)

System	$T_{\text{thermometry}}$ (°C)	$T_{\text{conductivimetry}}$ (°C)	Standard deviation
Paraffin PETROBRAS/RELAM ($C_{29}H_{60}$)	63.1	59.7	2.40
Turpentine (40% in mass) + $C_{29}H_{60}$	51.0	50.4	0.42
C_5 (50.25% in mass) + $C_{26}H_{54}$	39.0	37.9	0.78
C_6 (60.00% in mass) + $C_{26}H_{54}$	35.0	29.2	4.10
C_6 (75.45% in mass) + $C_{26}H_{54}$	30.5	28.3	1.56
Petroleum (Bahia)	36.5	26.3	7.21
	Average standard deviation		2.75

4. CONCLUSIONS

The experimental methodology presented in this work was very simple and quite satisfactory for the determination of the solidification and melting points of paraffins in light hydrocarbons and in crude oil. Both techniques, conductivimetry and thermometry, allow the determination of the solubility profiles of paraffins in light alkanes. The use of this technique remotely or in line may be a powerful tool for the prevention of wax deposition phenomena and optimization of the processes in the petrochemical industry.

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REFERENCES

Carnahan, N.F. Paraffin deposition in petroleum production. **Journal of Petroleum Technology** v. 41(11), p. 1024-1025, 1989.

Daubert, T. E., Danner, R. P. DIPPR Data Compilation Version 12.0 **AIChE**: New York, 1995.

Manning, F.S., Thompson, R.E. Oilfield processing Volume two: Crude oil. Tulsa. **Pennwell Books**. Volume 2. Chapter 2, 13-15, 1995.

Pan, C., Radosz, M. Modeling of solid–liquid equilibria in naphthalene. normal-alkane and polyethylene solutions. **Fluid Phase Equilibri**a, v. 155, p. 57-73, 1999.

Prausnitz, J.M., Lichtenthaler, R.N., Azevedo, E.G. Molecular thermodynamics of fluid phase equilibria. **Prentice-Hall**, 1986.

Provost, E., Chevallier, V., Bouroukba, M., Petitjean, D., Dirand, M. Solubility of some n-alkanes (C23.C25.C26.C28) in heptane. methylcyclohexane. and toluene. **Journal of Chemical Engineering Data**, v. 43, p. 745-749, 1998.

Tavares, E. C., Marcelino, S. I. S., Souza, C. P., Chiavone-Filho, O. Determination of Salt Solubility Data for Ternary Systems with a Quasiisothermic Thermometric Technique. **Thermochimica Acta**, v. 328, p. 253-258, 1999.

Tawer, R.D.C.A.N., Dick, G. Asphaltene deposition in production facilities. **SPE Production** Engineering, v. 5(4), p. 475-480, 1990.

Won, K.W. Thermodynamics for solid-liquid-vapor equilibria: wax phase formation from heavy hydrocarbon mixtures. **Fluid Phase Equilibria**, v. 30, p. 265-279, 1986.