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# Experimental Measurements and Thermodynamic Modeling of Paraffinic Wax Formation in Undercooled Solutions

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The crystallization of paraffinic materials from hydrocarbon mixtures subject to a cold environment is one of the problems faced by the petroleum industry. It can be found during oil production and in the transport and even in the use of refined materials such as diesels and fuels. A better understanding of the crystallization process and the capacity to model the wax formation would help to overcome this problem. This work is focused on the study of the two-phase region by developing a new experimental technique for measuring the composition of the phases in equilibrium and the amount of paraffins precipitating from a hydrocarbon mixture. The crystallization of several model systems, constituted by a mixture of normal alkanes between  $n\text{-C}_{19}\text{H}_{40}$  and  $n\text{-C}_{28}\text{H}_{58}$  dissolved in ethylbenzene in mass concentrations up to 25% weight, was promoted in an optical cell. The composition of the phases in equilibrium at several different temperatures below the cloud point was determined by chromatography. The amount of waxes formed and the cloud points were obtained by differential scanning calorimetry (DSC). The new technique is shown to be simple and accurate. Some particularities of paraffin crystallization were studied as well as the influence of aromatic compounds on the wax formation. A thermodynamic model was used to describe the measured data. It is based on the Flory-free-volume model for the liquid phase and on the predictive local composition model, a predictive form of the Wilson equation, for the nonideality of the solid solution. The model is shown to provide a good description of the SLE data for the studied systems.

## Introduction

Waxes are paraffinic compounds that precipitate from an oil or a fuel upon cooling. They can be found in all phases of the petroleum production and consumption cycle and constitute a nuisance whenever a hydrocarbon product, be it a crude or a fuel, is exposed to a cold environment during its transport or utilization. This fact motivates a great deal of experimental efforts, which in the last decade have been complemented with thermodynamic modeling, in the attempt to understand and describe the wax formation phenomenon. Most of this work has been concerned with the study of the temperature of appearance of the first paraffinic crystals, commonly known as the cloud point or wax appearance temperature. However, it is the amount of crystals formed that is responsible for the modification of the rheological properties of the solution, the formation of deposits, and the gelling of the hydrocarbon mixture, also known as the pour point. To be able to deal with the problems that arise with wax precipitation, the knowledge of the cloud points is not enough; for this reason, this work will be concerned with the study of the two-phase region.

Most of experimental techniques presented in the literature for the study of wax formation are mainly methods for the detection of the appearance of the first crystal or the study of its crystalline nature (Denicolo et al., 1984; Maroncelli et al., 1985; Ghogomu et al., 1989). Both for a better understanding of solid formation and for the development of thermodynamic models, it is of great interest to perform measurements in the two-phase region. Here a simple, yet accurate, experimental procedure is developed to study the composition of the phases in equilibrium below the cloud point. Synthetic mixtures of paraffins ranging from nonadecane to octacosane dissolved in ethylbenzene are placed

in a thermostatic bath and sampled at different temperatures. The composition of the phases in equilibrium is determined by chromatography. It is shown that the solid phase behavior in simple systems is ruled by an azeotrope-like equilibrium. The presence of multiple solid phases in complex mixtures is evidenced by the results from calorimetric (DSC) and chromatographic measurements combined. A study of the effect of aromatics on the wax formation is also performed, showing that they have no influence whatsoever in the solid appearance neither do they cocrystallize with the paraffinic material.

The data measured for seven paraffinic solutions is used to test the performance of the predictive local composition model (Coutinho et al., 1996; Coutinho and Stenby, 1996) for complex mixtures. The predictions are in good agreement with the experimental results.

## Experimental Measurements

The objective of this work is the development of a simple and accurate experimental procedure to measure the phase equilibrium below the cloud point temperature. Some data were available in the literature for cloud points in simple (Ghogomu et al., 1989; Ungerer et al., 1995) or complex systems (Darridon et al., 1996), yet no data were available to present for the composition of the phases in equilibrium and the amount of solid formed in the two-phase region.

Seven mixtures of paraffins were prepared from commercially available pure  $n$ -alkanes (Fluka with a purity of at least 99%). Each alkane was weighed in a 100 mL glass bottle and dissolved in a known mass of ethylbenzene (Aldrich, 99.8%) in the concentrations reported in Table 1. The solutions were then divided into five to ten vials containing each about 5 mL of solution. The vials were allowed to equilibrate at 240 K for 2 or 3 days. At this temperature at least 99% of the paraffinic material will be crystallized. They were

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**Table 1. Composition (Mass %) of the Paraffinic Solutions**

	sol I	sol II	sol III	sol IV	sol V	sol VI	sol VII
ethylbenzene	90.404	74.82	75.36	74.99	79.14	79.95	76.75
<i>n</i> -C14	0.452						
<i>n</i> -C19				12.49		3.340	3.207
<i>n</i> -C20						2.954	2.836
<i>n</i> -C21				12.52		2.565	2.463
<i>n</i> -C22	4.587	12.76				2.266	2.176
<i>n</i> -C23			11.14		16.20	2.000	1.918
<i>n</i> -C24	4.557	12.42	13.50		4.660	1.760	1.690
<i>n</i> -C25						1.541	1.480
<i>n</i> -C26						1.364	1.310
<i>n</i> -C27						1.198	1.152
<i>n</i> -C28						1.062	1.020
fluorene							3.998

introduced into a thermostatic bath and equilibrated at each temperature for 2 h before sampling. The temperature is increased between two samplings, promoting the melting of the solution in the vials rather than its crystallization. This reduces the problems associated with supercooled solutions and slow solid phase equilibration. Only one vial was sampled at each temperature. About 1 mL of liquid was taken with a syringe using a 0.450 mm filter to prevent the contamination of the sample by the crystals. The composition of the two samples obtained (the sampled liquid and the remaining liquid plus crystals:the precipitate) are measured by gas chromatography in a HP 5880 using a chromatographic column 2 m long and i.d. = 1/8 in., filled with 3% DEXIL 300 on Chromosorb WAW 80/100. Operating conditions: injector temperature, 623 K; detector temperature, 623 K; oven temperature program, initial temperature 373 K, initial time 2 min, heating rate 16 K/min, final temperature 573 K.

The composition of the actual solid phase is obtained by a mass balance that also provides the amount of solid phase present at that temperature (with the assumption that the solvent does not cocrystallize with paraffins). The concentration of paraffin *i* in the solid phase is given by

$$X_i^S = \frac{X_i^P - ZX_i^L}{1 - Z} \quad (1)$$

where  $X_i$  is the mass fraction of paraffin *i* and the superscripts S, P, and L represent respectively the solid phase (only the crystals), the precipitate (the remaining liquid plus crystals), and the liquid (filtrate). *Z* is obtained from

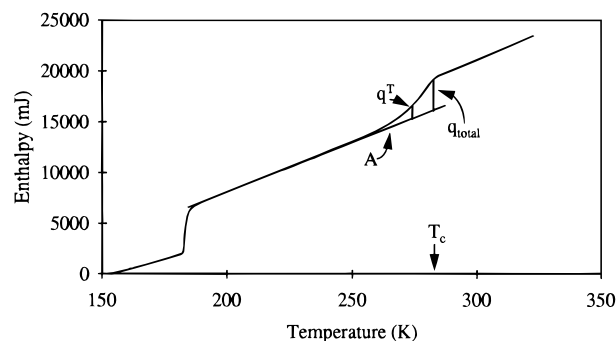
$$Z = \frac{X_{\text{solv}}^P}{X_{\text{solv}}^L} \quad (2)$$

where solv refers to the solvent (Van Winkle et al., 1987).

The fraction of total *n*-paraffins in the initial solution that has solidified,  $\alpha$ , is given by

$$\alpha = \frac{X^o - X^L}{X^S - X^L} \quad (3)$$

where the symbols have the meaning described before and the superscript o refers to the initial solution. This quantity can be calculated from the compositions of any mixture component, but the more correct values will be calculated for the solvent because in this case  $X^S = 0$ .

**Figure 1.** Description of the procedure to calculate the amount of paraffins crystallizing from a DSC curve.

The fraction of paraffins in the solid phase is calculated by dividing  $\alpha$  by the total mass fraction of paraffins present in the mixture:

$$\alpha_p = \frac{\alpha}{\sum_{\text{paraf}} X_i} \quad (4)$$

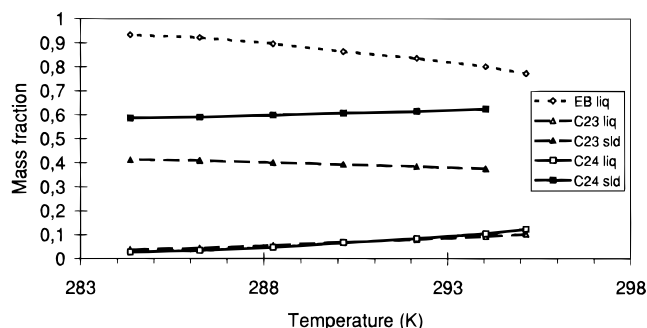
Aluminum pans of 150  $\mu\text{L}$  were filled to two-thirds with the seven solutions and analyzed in a Mettler TA 3000 differential scanning calorimeter (DSC) after being equilibrated for at least 48 h at 240 K. The DSC has a refrigeration system using liquid nitrogen that allows measurements to be done at temperatures below 150 K and provides a very good temperature control. The sample is heated from 150 to 320 K at a rate of 1 K/min. Fusion rather than crystallization was chosen for the reasons previously mentioned.

What is actually measured by DSC is not the amount of solid formed but the amount of solid melted at a given temperature. To measure this quantity, it is assumed that the fraction of melted solid is identical to the fraction of total heat used to melt it according to the following equation:

$$\alpha' = 1 - \alpha = \frac{\int_{T_m^{\text{EB}}}^T h_m^{\text{mix}} \frac{dm_{\text{mix}}}{dT} dT}{\int_{T_m^{\text{EB}}}^{T_c} h_m^{\text{mix}} \frac{dm_{\text{mix}}}{dT} dT} = \frac{q^T}{q_{\text{total}}} \approx \frac{m_{\text{p,liq}}^T}{m_{\text{p,total}}} \quad (5)$$

Since the composition of the solid changes during the melting, an approximation is introduced in the calculation. The results seem to show that the error introduced by this hypothesis is inferior to the experimental uncertainty itself and the data obtained from two independent measurement procedures (DSC and crystallization) agree quite well even for complex systems, as will be shown later.

To calculate the fraction of heat instead of the traditional DSC peaks, the energy used to heat the sample from 150 K to a given temperature *T* is used. This energy is obtained from the integration of the peaks and can be depicted as shown in Figure 1 where the calculation procedure is briefly described. A line A, tangent to the enthalpy curve just above the melting point of the solvent is drawn. It represents the energy required to heat the solution. The difference between this line and the enthalpic curve at a temperature *T*,  $q^T$ , is the energy used to melt the paraffins present in the liquid phase. At the cloud point the difference between these curves is the total energy required for the complete fusion of the paraffins in solution,  $q_{\text{total}}$ . The value



**Figure 2.** Experimental data for the temperature dependence of the phases compositions for solution III.

of  $\alpha$  can then be readily calculated for each temperature, giving the deposit curves presented. To use this calculation procedure, some hypotheses have to be made, namely that the excess heat capacities are insignificant, the heat capacities change with temperature is not important, and the difference heat capacities of the paraffins between the liquid and solid phases are negligible.

The DSC also provides the experimental values for the cloud point temperatures of the studied solutions.

## Results

Compositions of the seven solutions are presented in Table 1. The ternary mixtures I–V were used to verify the capacity of the apparatus in measuring the phase behavior below the cloud point. Cloud points for most of these systems had already been presented by Ghogmu et al. (1989) and they served to, through the use of the thermodynamic model later presented, indirectly study the precision of the experimental procedure adopted. An example of the experimental results is presented for the solution III in Figure 2. The experimental data measured are found in Tables 2–4 (for mixtures VI and VII they are available as Supporting Information). The behavior of the C23/C24/EB system (solution III) is typical of ternary systems. There is a regular decrease of the paraffin composition in the liquid phase with the heaviest alkane disappearing faster than the lightest. The solid phase is richer in the heaviest paraffin, and its concentration decreases as the lightest paraffin crystallizes. Figure 8 shows the results for the paraffinic solid fraction as a function of the temperature obtained both from chromatographic and calorimetric measurements. The paraffinic solid fraction is the fraction of the total amount of paraffins that are in the solid phase at a given temperature. The results obtained by the two methods agree well. It is interesting to notice that about 80% of the paraffins drop out of solution within 10 K below the cloud point and that within 30 K virtually all paraffins have crystallized, even if theoretically a small amount should always be in solution down to the melting point of ethylbenzene, around 170 K.

Some interesting features should be mentioned about the results for solutions VI and VII. The first is a solution of the ten normal alkanes ranging from nonadecane to octacosane in ethylbenzene and the latter results from the former by addition of some amount of the aromatic compound fluorene. There is a great difference between the DSC curves for these systems and those for the ternaries. The single peak characteristic of a single phase melting present in the ternaries is now replaced by a more complex curve with at least

two peaks, as shown in Figure 3. This is most probably an effect of the formation of multiple solid phases instead of a single solid solution with all the paraffins present. This is further supported by the results for the composition of nonadecane and fluorene in the solid phase of solution VII shown in Figure 4. (As will be shown later, the nonadecane compositional variation in the solid phase with temperature is identical for both solutions VI and VII.) The cloud point for these systems is about 290.5 K, as shown in Table 5. Yet no nonadecane is found in the solid phase down to 278 K. A similar behavior is presented by eicosane. This clearly shows that not all paraffins are present in the solid phase forming at the cloud point and that, according to the DSC results, another solid phase formed by lighter paraffins will appear at temperatures removed from the cloud point. While only X-ray diffraction measurements can definitely establish the number and nature of the phases forming, these results are a strong evidence of the presence of multiple solid phases, supporting the findings by other authors (Lira-Galeana et al., 1996; Gerson et al., 1991).

In the same figure it can be seen that within the investigated temperature region there is no aromatic precipitation. This is interesting and surprising given the concentration of the aromatic being larger than that of any of the paraffins. Also its melting temperature of 387.9 K is much larger than the 334.4 K of octacosane. It seems that the melting enthalpy (4 times larger for octacosane than for fluorene) plays a major role in promoting or preventing the crystallization of the components of a mixture. These data also indicate that, as expected, the crystallization of aromatics is independent of the paraffins creating another extra solid phase. Figures 5 and 6 present the data for the composition of the different paraffins in the solid phase and the amount of paraffinic material crystallized in solutions VI and VII. Since the data are identical in both systems within experimental uncertainty, the presence of an aromatic does not seem to have any influence on the paraffin crystallization.

## Thermodynamic Modeling

The modeling of SLE in this work will be done with a model that proved to be successful in the description of SLE in *n*-alkane systems.

**Liquid Phase  $g^E$  Model.** The nonideality of a hydrocarbon liquid phase arises from entropic effects such as size difference and free volume effects, and energetic interactions between unlike molecules such as aromatics and aliphatics. The Flory-free-volume equation can effectively deal with the first kind of interactions (Coutinho et al., 1995):

$$\ln \gamma_i^{\text{comb-h}} = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} \quad (6a)$$

with

$$\phi_i = \frac{x_i(V_i^{1/3} - V_{wi}^{1/3})^{3.3}}{\sum_j x_j(V_j^{1/3} - V_{wj}^{1/3})^{3.3}} \quad (6b)$$

where  $V_i$  is the molar volume, and  $V_{wi}$  is the van der Waals volume of component  $i$ .

**Table 2. Experimental Data for the Compositions in Both Phases and Fraction of Solid Paraffins for Solutions I and II**

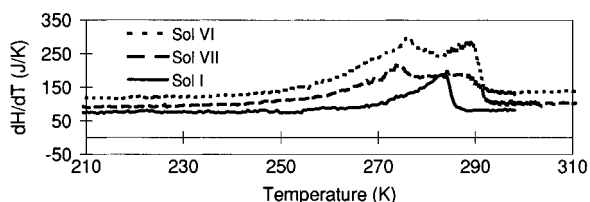
$T$ (K)	$W_{EBliq}$	$W_{C14liq}$	$W_{C22liq}$	$W_{C24liq}$	$W_{C14sld}$	$W_{C22sld}$	$W_{C24sld}$	$\alpha_p$
Solution I								
$> T_c$	0.9094	0.005 015	0.043 49	0.042 13				
281.2	0.9265	0.005 150	0.038 21	0.030 10	-0.005 597	0.3351	0.6885	0.2029
269.2	0.9413	0.005 082	0.032 92	0.020 66	0.002 309	0.3387	0.6584	0.3714
276.8	0.9523	0.005 410	0.027 51	0.014 76	0.001 535	0.3698	0.6247	0.4933
274.3	0.9608	0.005 734	0.023 55	0.009 902	-0.006 956	0.3965	0.6179	0.5856
272.5	0.9634	0.005 592	0.022 67	0.008 334	0.001 823	0.3933	0.6264	0.6135
Solution II								
$> T_c$	0.7647		0.1204	0.1149				
292.7	0.7746		0.1182	0.1073		0.3182	0.6818	0.0507
291.3	0.7976		0.1111	0.091 25		0.3389	0.6611	0.1640
289.4	0.8231		0.1014	0.075 43		0.3691	0.6309	0.2820
287.4	0.8429		0.095 49	0.061 58		0.3777	0.6222	0.3687
285.4	0.8716		0.083 99	0.044 43		0.3867	0.6133	0.4871
283.6	0.8884		0.076 71	0.034 86		0.3972	0.6028	0.5532

**Table 3. Experimental Data for the Compositions in Both Phases and Fraction of Solid Paraffins for Solutions III and V**

$T$ (K)	$W_{EBliq}$	$W_{C23liq}$	$W_{C24liq}$	$W_{C23sld}$	$W_{C24sld}$	$\alpha_p$
Solution III						
$> T_c$	0.7728	0.103 2	0.124 0			
294.1	0.8011	0.093 66	0.105 2	0.3760	0.6240	0.1432
292.2	0.8357	0.080 48	0.083 87	0.3853	0.6147	0.3050
290.2	0.8632	0.069 67	0.067 12	0.3936	0.6064	0.4248
288.3	0.8960	0.055 88	0.048 12	0.4014	0.5986	0.5578
286.3	0.9214	0.043 81	0.034 83	0.4100	0.5900	0.6542
284.4	0.9335	0.038 27	0.028 20	0.4135	0.5865	0.6985
Solution V						
$> T_c$	0.8049	0.1521	0.043 04			
290.9	0.8436	0.1222	0.034 16	0.7800	0.2200	0.2202
290.0	0.8642	0.1067	0.029 10	0.7715	0.2285	0.3289
288.1	0.8850	0.090 23	0.024 72	0.7762	0.2238	0.4342
285.6	0.9143	0.067 64	0.018 08	0.7744	0.2256	0.5736
283.1	0.9720	0.022 34	0.005 688	0.7794	0.2206	0.8241

**Table 4. Experimental Data for the Compositions in Both Phases and Fraction of Solid Paraffins for Solution IV**

$T$ (K)	$W_{EBliq}$	$W_{C19liq}$	$W_{C21liq}$	$W_{C19sld}$	$W_{C21sld}$	$\alpha_p$
$> T_c$	0.7572	0.1223	0.1206			
280.5	0.7756	0.1191	0.1053	0.2008	0.7992	0.0951
280.1	0.7800	0.1174	0.1027	0.2825	0.7175	0.1169
277.7	0.8013	0.1132	0.08551	0.2768	0.7232	0.2203
275.5	0.8305	0.1039	0.06560	0.2970	0.7030	0.3533
273.4	0.8602	0.09216	0.04765	0.3445	0.6555	0.4791

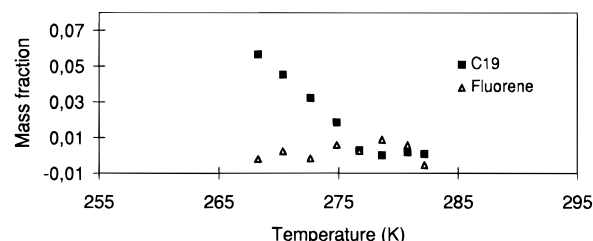
**Figure 3.** DSC measurements for solutions I, VI, and VII.

According to what was done in previous works (Kontogeorgis et al., 1993; Coutinho and Stenby, 1996), the modified UNIFAC residual term was added to the combinatorial-free-volume term without parameter re-estimation. The Gibbs free energy model used for the liquid phase can thus be described as

$$\ln \gamma = \ln \gamma^{\text{res}} + \ln \gamma^{\text{comb-fv}} \quad (7)$$

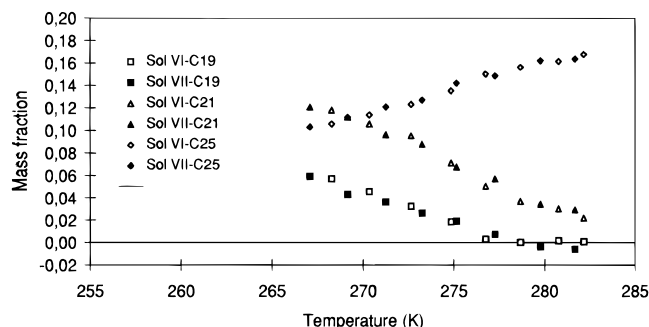
where  $\ln \gamma^{\text{comb-fv}}$  is described by eqs 6a and 6b and  $\ln \gamma^{\text{res}}$  is given by modified UNIFAC (Fredenslund et al., 1977; Hansen et al., 1991).

**Solid Phase  $g^E$  Model.** For the description of the nonideality of orthorhombic solid phases a predictive

**Figure 4.** Experimental data for the temperature dependence of the compositions of C19 and fluorene in the solid phase for solution VII.**Table 5. Cloud Point Temperatures for Multicomponent Paraffin Mixtures**

	paraffins	$T_c(\text{exp})$ (K)	$T_c(\text{model})$ (K)	$\Delta T$ (K)
solution VI <sup>a</sup>	EB, C19 to C28	$290.8 \pm 0.2$	291.1	0.3
solution VII <sup>a</sup>	EB, Flrn, C19 to C28	$291.1 \pm 0.2$	291.1	0.0
mixture A <sup>b</sup>	C10 + C20 to C30	$293.3 \pm 0.3$	294.3	1.0
mixture B <sup>b</sup>	C10 + C18 to C30	$298.7 \pm 0.3$	299.3	0.6
mixture C <sup>b</sup>	C10 + C18 to C27	$296.8 \pm 0.3$	296.9	0.1
mixture D <sup>b</sup>	C10, C18, C30	$313.2 \pm 0.3$	312.6	0.6

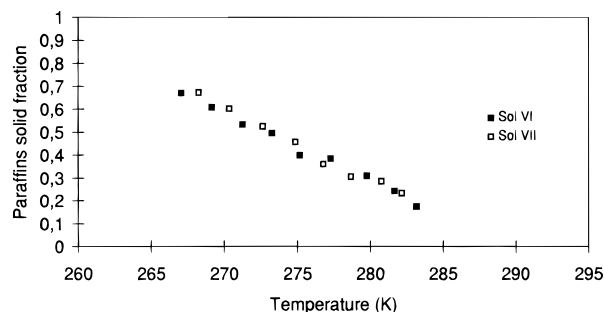
<sup>a</sup> This work. <sup>b</sup> Darridon et al. (1996).

**Figure 5.** Comparison between the results for the fraction of crystallized paraffins for solutions VI and VII.

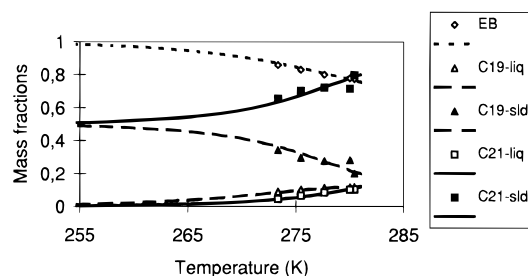
version of the Wilson equation developed by Coutinho et al. (1996) is used. The model is basically a version of the Wilson equation where local mole fractions instead of local volumetric fractions are employed, as shown in eq 8.

$$\frac{g^E}{RT} = - \sum_{i=1}^m x_i \ln \left[ \sum_{j=1}^m x_j \exp \left( - \frac{\lambda_{ij} - \lambda_{ii}}{RT} \right) \right] \quad (8)$$

The pair interaction energies,  $\lambda_{ii}$  and  $\lambda_{ij}$ , are obtained from physical considerations relating the molecular interactions with macroscopic properties. The proce-



**Figure 6.** Comparison between the experimental temperature dependence for the compositions in the solid phase between solutions VI and VII.



**Figure 7.** Experimental data and modeling results for the temperature dependence of the phase compositions for solution IV.

ture for calculation of interaction energies is summarized in eqs 9a and 9b:

$$\lambda_{ii} = -\frac{2}{Z}(\Delta h_{\text{sblm}_i} - RT) \quad (9a)$$

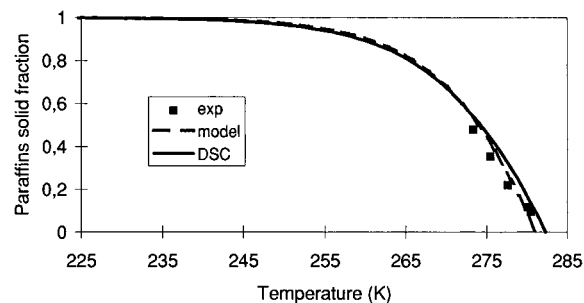
where  $Z$  is the coordination number (Coutinho et al., 1996) and  $\Delta h_{\text{sblm}}$  is the enthalpy of sublimation of the pure  $n$ -alkanes.

$$\lambda_{ij} = \lambda_{ii} \quad (9b)$$

where  $i$  is the  $n$ -alkane with the shorter chain of the pair  $ij$ .

This approach provides a predictive model where only the pure component thermophysical properties are required. This very successfully described the cloud point temperatures for the ternary systems  $n\text{-C}_{22}\text{H}_{46}/n\text{-C}_{24}\text{H}_{50}$ /ethylbenzene and  $n\text{-C}_{23}\text{H}_{48}/n\text{-C}_{24}\text{H}_{50}$ /ethylbenzene within the uncertainty of the experimental data (Coutinho and Stenby, 1996). It was then expected that it would provide a good description of the liquid phase compositions and the amount of solid material forming in solutions I–IV because the former is directly obtained from the cloud point surface and the latter is obtained from the same surface using the lever rule. Thus a good agreement between the experimental data and the model supports the accuracy of the experimental method adopted since it establishes an indirect comparison between the data measured in this work and the data by Ghogomu et al. (1989). Only the outcome for the solid phase compositions was ignored.

The description of all the ternary systems measured is very good for both the composition of the liquid phase and the fraction of solid paraffins. Examples are presented in Figures 7 and 8 for solution IV; the same results are obtained for solution V. They thus ascertain the capacities of the proposed experimental technique. In what concerns the solid phase, the modeling is not always as successful as that presented in these figures. This is not unexpected given the results of the model



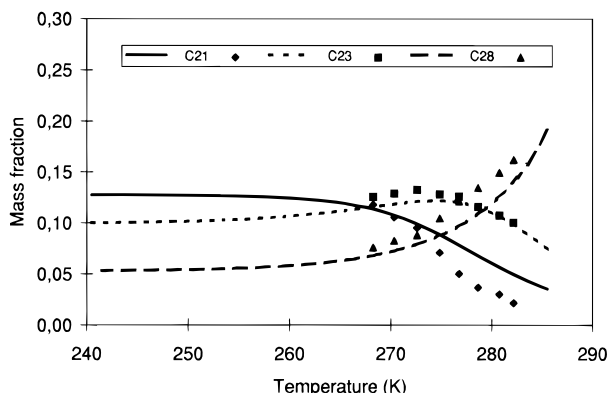
**Figure 8.** Experimental data and modeling results for the fraction of paraffins in the solid phase for solution IV.

**Table 6.** Comparison of the Paraffins Concentration Ratio in the Liquid and Solid Phases for Solution V

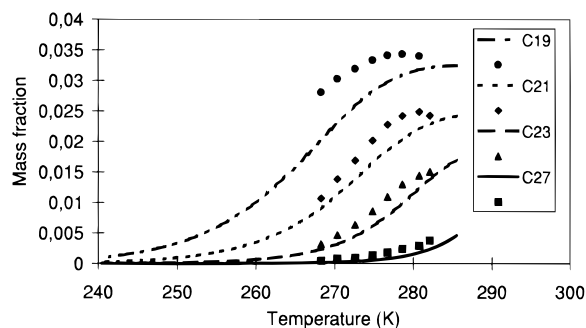
$T$ (K)	$W_{C23}/W_{C24}$
> 292.2 (liquid phase)	3.481
292.2	3.858
288.2	3.611
284.2	3.527
280.2	3.495
275.2	3.481

for the phase diagrams of two paraffins (Coutinho et al., 1996). The results for solution V are by all means similar to those previously described in what concerns the variation of the composition of the phases with temperature and the amount of solid formed expressed as the fraction of paraffinic material that has not crystallized. The model provides a very good description of the experimental data for all phases, and the amount of solid formed. Solution IV is somewhat more interesting. Unlike the results previously presented, and in particular those of Figure 2 for solution III that is composed of the same paraffins, the solid phase composition of tricosane, the light alkane, decreases with temperature while a slight increase is found for tetracosane. This peculiar phenomenon is better expressed by the ratio of the compositions of the two paraffins presented in Table 6, showing that the solid phase is richer than the liquid phase in the lightest compound! This can only be explained on the basis of an azeotrope-like behavior for the solid phase. A look into the experimental phase diagram for  $n\text{-C}_{23}\text{H}_{48}/n\text{-C}_{24}\text{H}_{50}$  (Denicolo et al., 1984) helps to clarify the situation. The orthorhombic phase does present an azeotropic behavior for this system. This result supports the view expressed in a previous work that the lowering of the cloud point in the presence of a second alkane was due to an azeotropic behavior of paraffinic solutions and not to poor crystal formation (Coutinho and Stenby, 1996).

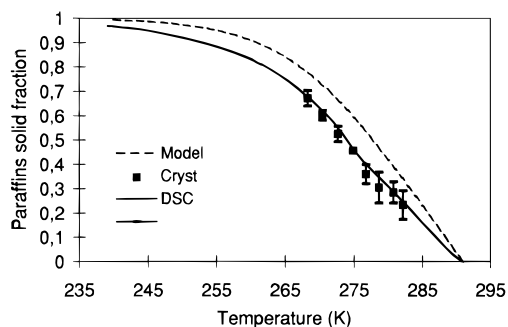
As previously discussed, all evidence indicates the presence of multiple solid phases in the crystals formed from solutions VI and VII. The Wilson equation is unable to describe partial miscibility since the second derivative on the Gibbs energy of mixing on the composition will never be negative (Prausnitz et al., 1986). This means that the predictive local compositional model based on the Wilson equation will be unable to deal with the multiphasic behavior evidenced experimentally. Nevertheless the modeling of these systems using the presented model was attempted by considering the formation of a single solid phase where all the paraffins in solution would be present. For solution VII the modeling was done by preventing the crystallization of fluorene since another solid phase would have to be used for the aromatic. As expected, the results are not as good as for the ternary systems and an important



**Figure 9.** Experimental data and modeling results for the temperature dependence of the solid phase composition for solution VII.



**Figure 10.** Experimental data and modeling results for the temperature dependence of the liquid phase composition for solution VII.



**Figure 11.** Experimental data and modeling results for the fraction of crystallized paraffins for solution VII.

error is obtained for the compositions of the lightest components since crystallization at the cloud point is incorrectly assumed for them. The composition of the higher alkanes is, however, fairly described both qualitatively and quantitatively in the solid phase, as can be seen in Figure 9 for solution VII, the same results are obtained for solution VI. It is interesting to notice that light, intermediate, and heavy alkanes exhibit different behaviors for the solid phase composition variation with the temperature. As expected, not much difference exists between the results for the two solutions. Since an early precipitation is assumed for some of the components, the compositions in the liquid phase are somewhat underestimated, in particular for the light components like nonadecane, as shown in Figure 10. For the same reason the amount of paraffins crystallizing is also slightly overestimated, as presented in Figure 11. The cloud point temperatures are, however, very well predicted because they are mainly dependent on the behavior of the heaviest molecules and not on the

lightest. As shown in Table 5, the predicted cloud point temperatures for solutions VI and VII as well as for four other paraffinic mixtures by Darridon et al. (1996) have an average error of about 0.5 K, which should be close to the experimental uncertainty.

Considering that these results are pure predictions and the assumption of a single solid phase, known to be inappropriate, is used, the results are surprisingly good. The model appears to be able to deal with complex systems, and the introduction of multiple solid phases in the modeling should help to further improve the predictions.

## Conclusions

A simple, yet accurate, experimental procedure for measuring solid liquid equilibria below the cloud point in alkane/hydrocarbon systems is presented. Using this method, experimental data for seven paraffinic systems were measured. The results foster the understanding of hydrocarbon solid phase formation from solution. They provide strong evidence for the formation of multiple solid phases in alkane crystals and show that fluorene does not cocrystallize with paraffins nor changes their crystallization behavior. The predictive LCM model was applied to the description of the measured data. The ternary systems were successfully modeled. The results obtained in the description of complex systems were quite surprising for pure predictions in spite of the assumption of a single solid phase imposed by the limitations of the Wilson equation. With the exception of the lightest compounds (nonadecane and eicosane) the compositions in both phases were described with an acceptable accuracy and the cloud point temperatures are predicted within the experimental uncertainty.

## Acknowledgment

The authors would like to acknowledge the collaboration of S. Calange in the calorimetric measurements and L. Barré during the development of the crystallization technique.

**Supporting Information Available:** Experimental data for the compositions in both phases and fraction of solid paraffins for mixtures VI and VII (two tables) (4 pages). Ordering information is given on any current masthead page.

## List of Symbols

$g$  = Gibbs free energy  
 $h$  = enthalpy  
 $m$  = weight of paraffin  
 $q$  = quantity of energy  
 $R$  = universal gas constant  
 $T$  = temperature  
 $V$  = molar volume  
 $V_w$  = van der Waals volume  
 $X$  = mass fraction  
 $x$  = liquid phase molar fraction  
 $Z$  = coordination number  
 $Z$  = parameter defined in eq 2

## Greek Letters

$\alpha$  = fraction of crystallized material  
 $\gamma$  = activity coefficient  
 $\lambda$  = pair interaction energy

*Subscripts*

c = cloud point  
*i* = component *i*  
*j* = component *j*  
 liq = liquid  
 m = melting  
 mix = mixture  
 p = paraffins  
 sbm = sublimation  
 total = total

*Superscripts*

E = excess property  
 L = liquid  
 P = precipitate  
 S = solid  
 T = temperature *T*

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Received for review December 23, 1996

Revised manuscript received June 5, 1997

Accepted June 11, 1997\*

IE960817U

\* Abstract published in *Advance ACS Abstracts*, August 15, 1997.