

# Measuring the Amount of Crystallinity in Solutions Using DSC

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The amount of solid that forms in a solution at temperatures below the cloud point, is an important quantity in the design of crystallisation processes. A new method using differential scanning calorimetry (DSC) to measure the fraction of crystallised solution,  $\alpha_{solution}^S$ , is proposed. A very good agreement is obtained between the data measured by the new calorimetric method and using alternative techniques. A simple graphic version of the calculation procedure is also presented. It is shown to produce quick and fair estimates for the solid fraction by a simple analysis of a plot of enthalpy variation with temperature.

La quantité de solides qui se forme dans une solution à des températures au-dessous du point de trouble est un facteur important dans la conception des procédés de cristallisation. On propose une nouvelle méthode utilisant la calorimétrie différentielle à balayage (DSC) afin de mesurer la fraction de solution cristallisée,  $\alpha_{solution}^S$ . Un très bon accord est obtenu entre les données mesurées par la nouvelle méthode calorimétrique et d'autres techniques utilisées. On version graphique simple de la procédure de calcul est également présentée. On montre qu'elle peut produire des estimations rapides et fiables pour la fraction de solides par simple analyse d'un tracé de variation d'enthalpie avec la température.

Keywords: solid-liquid equilibrium, calorimetry, DSC, crystallisation.

The knowledge of the amount of solid precipitating from a solution is required in designing and operating plants where either crystallisation is promoted for purification purposes or when solid formation is to be prevented, as for instance with the wax deposition problem. For simple systems when the phase diagram is known the evaluation of the fraction of precipitated material can be readily obtained by means of a simple calculation. However this is not the case when dealing with complex mixtures for which neither experimental phase diagrams nor calculation procedures exist to estimate the amount of precipitate being formed at a given temperature. For those systems this quantity can only be assessed experimentally.

To evaluate the quantity of precipitated forming at a given temperature a crystallisation of the solution problem can be performed measuring directly or indirectly the fraction of solid material (Van Winkle et al., 1987; Coutinho and Ruffier-Meray, 1997), but this is time consuming and may be a difficult technique if the phases do not separate easily. An alternative method would be the use of the Differential Scanning Calorimetry (DSC). This is a well known technique but its use for measuring solid fractions is not well understood and seldom used. The procedure presented in some DSC manuals for these measurements is poorly accurate and, to a large extent, empirical. In this work a new methodology for such measurements, along with its thermodynamical background, will be presented. The assumptions and simplifications used in the derivation of the equations are thoroughly stated and from them the limits of applicability of the technique inferred. Calorimetric measurements of the fraction of solidified solution, for both simple and complex organic systems with single or multiple solid phases, are made and compared with data for the same systems measured using alternative techniques. The good

agreement between the data obtained by the different methods show the validity of the procedure here proposed. The applicability of this method to a solution of organic or inorganic compounds requires only that the thermophysical properties of solutes and solvent conform to the simplifications adopted on the development of the expressions used in the calculations, presented in the next section.

## Thermodynamical background

Instead of the fraction of solution crystallised,  $\alpha_{solution}^S$ , the thermodynamical derivation will focus in the fraction of solute melted,  $\alpha_{slt}^L$ , these two quantities being related by Equation (1):

$$\alpha_{solution}^S = \frac{m_{solution}^S}{m_{solution}^{total}} = (1 - \alpha_{slt}^L) * \sum_i W_{sli} \dots \dots \dots (1)$$

Where  $W_{sli}$  is the mass fraction of solute  $i$  in the mixture. Hereafter  $\alpha_{slt}^L$  is noted  $\alpha^L$  to simplify the notation. The reader not interested in the theory behind the proposed technique should go straight to Equation (10).

It will be considered the melting of a frozen mixture of  $n$  solutes in a single solvent from a temperature  $T_o$  below the solvent melting temperature to complete fusion of the mixture. The solutes may or may not form solid solutions. It is attempted to measure:

$$\alpha^L = \frac{\sum_i \int_{T_m}^T \frac{dm_{sli}^L}{dT} dT}{\sum_i \int_{T_m}^{T_c} \frac{dm_{sli}^L}{dT} dT} = \frac{\sum_i m_{sli}^L}{\sum_i m_{sli}^{total}} \dots \dots \dots (2)$$

Where  $T_c$ , the cloud point temperature, is the temperature of disappearance of the last crystals. However, using a

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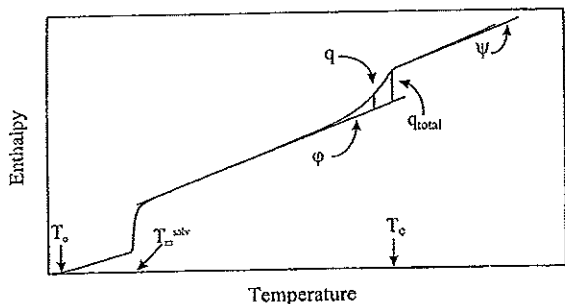


Figure 1 — Description of the application of the graphical calculation procedure to the curve of the enthalpy variation with temperature.

calorimeter only enthalpic rather than mass variations can be accounted for. What can be measured by DSC is the ratio between the energy  $q(T)$ , required to melt the fraction of the solutes present in the liquid phase at temperature  $T$ , and the energy required to completely melt the solutes ( $q_{total}$ ):

$$\alpha^{L'} = \frac{\sum_i \int_{T_m^{sol}}^T h_m^{sli}(T) \frac{dm_{sli}^L}{dT} dT}{\sum_i \int_{T_m^{sol}}^{T_c} h_m^{sli}(T) \frac{dm_{sli}^L}{dT} dT} = \frac{q(T)}{q_{total}} \quad \dots \dots (3)$$

The fractions  $\alpha^L$  and  $\alpha^{L'}$  are different but there are two cases when the identity between them can be established: the first is when the heats of melting for the different solutes are similar and may be considered temperature independent in the temperature range under analysis, this occurs for paraffinic waxes or for a mixture of sugars; the second case is not as evident but more useful, the identity is verified for temperatures not far removed from the cloud point,  $T_c$ . It is simple to show that as  $T$  approaches  $T_c$ ,  $\alpha^{L'} \rightarrow \alpha^L$ . This is a very interesting result since in many cases most of the solute crystallises within a narrow temperature range below the cloud point making possible to use the measurement of  $\alpha^{L'}$  for  $\alpha^L$ .

Unfortunately it is not possible to directly access the energies defined as  $q(T)$  and  $q_{total}$  by means of a DSC measurement. Beside the heat used for melting the solute, the energy for heating the solution and heat effects associated to the mixing in the liquid phase are also being measured. It is thus necessary to isolate the energy used for melting the solute from the others. To calculate the heat fraction defined by Equation (3), data of the enthalpy variation of a solution between an initial temperature  $T_c$ , where the solution is completely solidified, and a temperature  $T$  above the cloud point are used. An example of such data is presented in Figure 1. Its mathematical expression is:

$$h(T) = h^A(T < T_m^{sol}) + h^B(T = T_m^{sol}) + h^C(T_m^{sol} < T \leq T_c) + h^D(T_c < T) \quad \dots \dots (4)$$

With

$$h^A = m_{sol}^{total} \int_{T_c}^T C_{p_{sol}}^S dT + \sum_i m_{sli}^{total} \int_{T_c}^T C_{p_{sli}}^S dT \quad \dots (5)$$

$$h^B = m_{sol}^{total} h_m^{sol} \langle T_m^{sol} \rangle \quad \dots \dots (6)$$

$$h^C = m_{sol}^{total} \int_{T_m^{sol}}^T C_{p_{sol}}^L dT + \sum_i \int_{T_m^{sol}}^T m_{sli}^S C_{p_{sli}}^S dT + \sum_i \int_{T_m^{sol}}^T m_{sli}^L C_{p_{sli}}^L dT + \sum_i \int_{T_m^{sol}}^T h_{mi}^{sli} \frac{dm_{sli}^L}{dT} dT + \left( m_{sol}^{total} + \sum_i m_{sli}^L \right) h_{liq}^E + \left( \sum_i m_{sli}^S \langle T \rangle h_{sld}^E - \sum_i m_{sli}^{total} \langle T_m^{sol} \rangle h_{sld}^E \right) \quad \dots \dots (7)$$

$$h^D = m_{sol}^{total} \int_{T_c}^T C_{p_{sol}}^L dT + \sum_i m_{sli}^{total} \int_{T_c}^T C_{p_{sli}}^L dT \quad \dots \dots (8)$$

The effects due to the excess heat capacities in both phases are neglected. They are too small comparing to the others and normally inferior to the sensibility of the measurements.

To measure  $\alpha^L$  an auxiliary quantity,  $I(T)$ , is used. It represents the energy required to heat the mixture from the solvent melting point to the temperature  $T$  and the heat effects associated to the solutes and solvent liquid and solid phases mixing. It is described by:

$$I(T) = h \langle T_m^{sol} \rangle + m_{sol}^{total} \int_{T_m^{sol}}^T C_{p_{sol}}^L dT + \sum_i \int_{T_m^{sol}}^T m_{sli}^S C_{p_{sli}}^S dT + \sum_i \int_{T_m^{sol}}^T m_{sli}^L C_{p_{sli}}^L dT + \left( m_{sol}^{total} + \sum_i m_{sli}^L \right) h_{liq}^E + \left( \sum_i m_{sli}^S \langle T \rangle h_{sld}^E - \sum_i m_{sli}^{tot} \langle T_m^{sol} \rangle h_{sld}^E \right) \quad \dots \dots (9)$$

Using the energy line  $I(T)$ , Equation (3) can be represented in terms of the measured quantities by:

$$\alpha^L = \frac{h(T) - I(T)}{h(T_c) - I(T_c)} \quad \dots \dots (10)$$

To estimate  $I(T)$  from the measured data a straight line  $\phi$ , tangent to the curve  $h(T)$  just above the melting point of the solvent is drawn. It represents the energy required to heat the liquid solvent and the solid solutes at temperatures above the melting point of the solvent:

$$\phi(T) = h \langle T_m^{sol} \rangle + \left( m_{sol}^{total} C_{p_{sol}}^L \langle T_m^{sol} \rangle + \sum_i m_{sli}^{total} C_{p_{sli}}^S \langle T_m^{sol} \rangle \right) (T - T_m^{sol}) \quad \dots \dots (11)$$

Another straight line,  $\psi$ , tangent to the enthalpy curve  $h(T)$ , just above the temperature of disappearing of the last crystal,  $T_c$ , is drawn. It represents the energy used to heat the solution above the cloud point temperature:

$$\psi(T) = h(T_c) + \left( m_{\text{sol}}^{\text{total}} C_{p,\text{sol}}^L \langle T_c \rangle + \sum_i m_{\text{sl}}^{\text{total}} C_{p,\text{sl}}^L \langle T_c \rangle \right) (T - T_c) \quad (12)$$

If the heat capacities are considered to be temperature independent, it is possible to show that:

$$\frac{dI}{dT} = \alpha^L \left( \frac{d\psi}{dT} - \frac{d\phi}{dT} \right) + \frac{d\phi}{dT} + m_{\text{sl}}^{\text{total}} \frac{d\alpha^L}{dT} (h_{\text{liq}}^E - h_{\text{sl}}^E) + m_{\text{liq}}^{\text{total}} \langle T \rangle \frac{dh_{\text{liq}}^E}{dT} + m_{\text{sl}}^{\text{total}} \langle T \rangle \frac{dh_{\text{sl}}^E}{dT} \quad (13)$$

The last three terms simplify if the liquid solution is athermal and there is no solid solution. Even when this is not verified, if the liquid and solid phases present the same kind of deviations to the ideality in what concerns the excess enthalpy these terms will compensate each other, strongly decreasing their importance. Whenever the excess enthalpy effects can be neglected Equation (13) reduces to:

$$\frac{dI}{dT} = \frac{d\phi}{dT} + \alpha^L \left( \frac{d\psi}{dT} - \frac{d\phi}{dT} \right) \quad (14)$$

and the estimation of  $\alpha^L$ , as described hereafter, is straightforward.

Using the slopes of the lines  $\phi$  and  $\psi$  the numerical integration of  $dI/dT$  can be performed and a simple iterative procedure leads to the value of  $\alpha^L$ . The assumption, made above, of temperature independent heat capacities affects only the term  $(d\phi/dT - d\psi/dT)$ . However the slopes of the two straight lines are usually not very different. Moreover  $\alpha^L$  ranges from 0 to 1 further reducing its effect. In the studied systems this assumption never affects the value of  $dI/dT$  by more than 2% and its influence in the estimation of  $\alpha^L$  is inferior to 0.1% for  $\alpha^L > 0.01$ .

When the slopes of  $\phi$  and  $\psi$  do not differ more than 20%, Equation (14) can further simplify reducing to  $I = \phi$ . This simplification would introduce a relative error inferior to 2.5% in  $\alpha^L$  for  $\alpha^L > 0.01$  and would allow the fraction of melted solute to be calculated from a simple graphical construction. Since  $I = \phi$ , the numerator of Equation (10) is just the distance between the enthalpy curve,  $h(T)$ , and the straight line  $\phi$  at a given temperature. Similarly the denominator is the distance between the enthalpy curve and the line  $\phi$  at the temperature of disappearance of the last crystal  $T_c$ . The fraction of solute melted,  $\alpha^L$ , is thus simply given by the ratio of the distance between the enthalpy curve and the straight  $\phi$  measured at a temperature  $T$  and the same distance measured at  $T_c$  as shown in Figure 1. This gives a simple and fast method to estimate the amount of solid crystallising at a given temperature once a calorimetric measurement as been performed.

Examples of the use of the proposed method and its graphical version, for estimation of the amount of solid phase being formed in binary and multicomponent hydrocarbon

mixtures, are presented in the next section and the results compared with data measured by alternative techniques.

## Experimental measurements

### CALORIMETRIC MEASUREMENTS

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%).

Aluminium pans of 150  $\mu\text{L}$  were filled up to 2/3 with the mixtures under study and were analysed in a Mettler TA 3000 Differential Scanning Calorimeter (DSC) after being equilibrated for at least 2 days at 240 K. At this temperature at least 99% of the paraffinic material will be crystallised and this equilibration will reduce the problems associated to non-equilibrium in the solid phase. The DSC has a refrigeration system using liquid nitrogen that allows measurements to be done at temperatures down to 150 K and provides a very precise temperature control. The sample is cooled from 240 to 150 K in the calorimeter and, after equilibration, heated from 150 K up to 320 K at a rate of 0.5 K/min. The use of a low heating rate is very important to assure an equilibrium state during the heating. Fusion rather than crystallisation is chosen to avoid undercooling of the solution and problems of solid phase non-equilibrium. The enthalpy changes were registered every 0.1 K between the starting and final temperatures and treated according to the procedure shown in the previous section to evaluate the fraction of crystallised solution  $\alpha^{\text{solution}}$ .

### CRYSTALLISATION AND CHROMATOGRAPHIC MEASUREMENTS

The hydrocarbon mixtures were divided by five to ten vials containing each about 5 ml of solution. Like the DSC pans the vials were also equilibrated at 240 K for 2 or 3 days. They were introduced into a thermostatic bath and equilibrated at the lowest temperature for 2 hours before sampling. About 1 mL of liquid phase was sampled from one of the vials using a syringe with a 450 nm filter to prevent the contamination of the liquid by the crystals. The temperature was then increased of about 2 K and after a new equilibration of another 2 hours another vial is sampled. The process is repeated for each vial producing two samples per vial: one of liquid and the other of precipitated material (solid with entrapped liquid). The composition of the samples are measured by gas chromatography in a HP 5880 using a chromatographic column 2 m long and ID = 3/8 mm (1/8 in.), filled with 3% DEXIL 300 on chromosorb WAW 80/100. Using the measured compositions, the fraction of solute crystallised at each temperature are easily calculated by a mass balance (Van Winkle et al., 1987; Coutinho and Ruffier-Meray, 1997).

## Results

Three hydrocarbon solutions were studied: a binary with a single solute, docosane, a ternary with two solutes and a mixtures of ten n-alkanes and an aromatic compound, fluorene. For all the solutions the solvent is ethylbenzene. Their compositions are presented in Table 1 together with the thermophysical properties of the compounds. The heats of

TABLE I  
Composition (mass %) of the Studied Solutions and Thermophysical Properties of the Pure Compounds

	Sol I	Sol II	Sol III	$^a T_m$ (K)	$^a T_{tr}$ (K)	$^a H_m$ (kJ/mol)	$^a H_{tr}$ (kJ/mol)
Ethylbenzene	78.56	75.36	76.75	178.2		9.184	
n-C19			3.207	305.2	295.2	45.845	13.816
n-C20			2.836	310.0	300.2	46.561	15.596
n-C21			2.463	313.4	305.7	47.729	15.491
n-C22	21.44		2.176	317.2	309.4	50.803	19.305
n-C23		11.14	1.918	320.7	313.2	52.900	22.048
n-C24		13.50	1.690	323.8	317.3	55.014	23.647
n-C25			1.480	326.7	320.2	57.778	26.084
n-C26			1.310	329.5	324.0	59.536	26.620
n-C27			1.152	332.0	326.2	60.457	28.973
n-C28			1.020	334.4	329.7	64.058	29.123
Fluorene			3.998	387.9		19.580	

<sup>a</sup> data extracted from Broadhurst (1962).

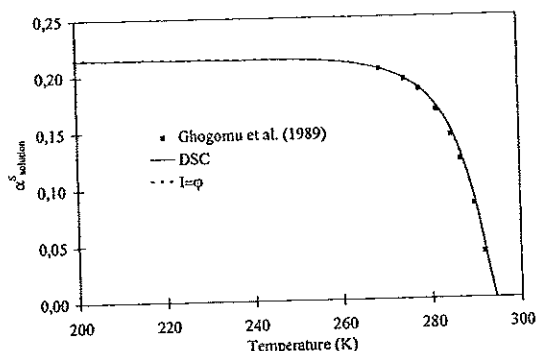


Figure 2 — Comparison between the fraction of crystallised solution measured by the proposed method and the data by Ghogomu et al. (1989) for Solution I ( $n\text{-C}_{22}\text{H}_{46}$ /ethylbenzene).

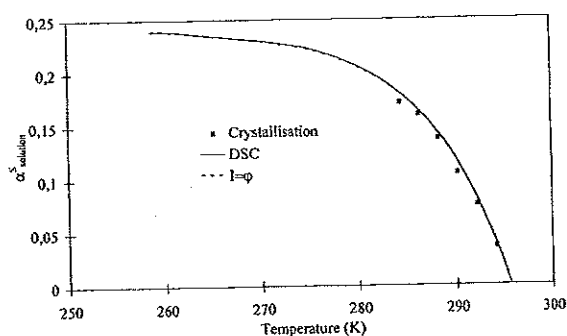


Figure 3 — Comparison between the fraction of crystallised solution measured by the proposed method and the crystallisation technique described in the text for Solution II ( $n\text{-C}_{23}\text{H}_{48}/n\text{-C}_{24}\text{H}_{50}$ /ethylbenzene).

melting of the compounds that co-crystallise are not very different but the possibility of using  $\alpha^{L'}$  for  $\alpha^L$  arises mainly from the crystallisation of most of the solute occurring in a narrow temperature range below the cloud point as is manifest from Figures 2 to 4. The excess enthalpies for all these mixtures present positive deviations to the ideality in both the liquid and solid phases. For the binary, the solid fractions measured by calorimetry are compared with those calculated from the phase diagram presented by Ghogomu et al. (1989). For the two other mixtures the solid fractions

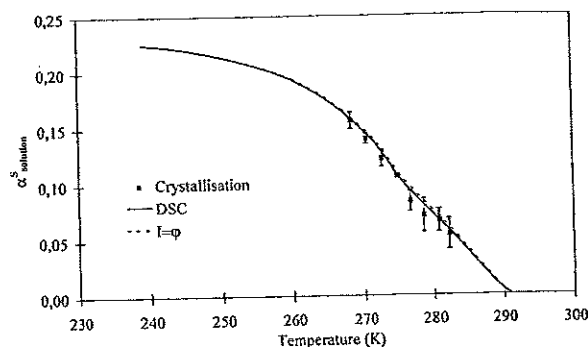


Figure 4 — Comparison between the fraction of crystallised solution measured by the proposed method and the crystallisation technique described in the text for a mixture of hydrocarbons in ethylbenzene (Solution III).

TABLE 2  
Slopes of the Lines  $\phi$  and  $\psi$  (mJ/mol·K)

	Solution I	Solution II	Solution III
line $\phi$	92.51	58.36	90.65
line $\psi$	100.11	69.40	102.41

were determined by crystallisation as described before. The results are presented in Figures 2 to 4. For all the mixtures there is a very good agreement between the data obtained by the two different procedures giving a good indication about the capacities of the proposed method to measure the solid fractions. It is interesting to notice the inflexion point presented by the DSC curve and the crystallisation data in Figure 4, due to the presence of multiple solid phases in Solution III (Coutinho and Ruffier-Meray, 1997). Moreover, in spite of the very large values for the excess enthalpy in the solid phase presented by these systems (Maroncelli et al., 1985; Wurflinger and Schneider, 1973; Haget, 1996) the assumption that the last terms of Equation (13) are negligible does not seem to introduce a significant error in the measurements.

In the figures are also presented the results obtained from the graphical method described before. As shown in Table 2 the slopes of the tangents  $\phi$  and  $\psi$  are close enough to make  $I = \phi$ . The results presented clearly indicate that the errors introduced in the estimation of the solid fractions by the

graphical method are unimportant. This method is of much simpler and faster utilisation, and it can replace the iterative calculation procedure when the slopes of the tangents are similar or when the required accuracy for the estimation of the solid fraction is not too high.

The method here presented, based in the curve of the enthalpy variation to measure the solid fraction forming in a solution upon cooling, is much more accurate and less empirical than the classical method where a fairly arbitrary baseline is chosen to perform the peaks integration and an average enthalpy of fusion is used introducing a large uncertainty in the determinations. The knowledge of the thermodynamic background behind these measurements helps to understand the limits of applicability and the reliability of the method. The results presented show that when the mixtures under study conform to the assumptions made in the derivation of the theory, the method can be very accurate. Moreover when the accuracy requirements are not very stringent, the simple geometric construction presented in Figure 1 can produce quick and fair estimates for the solid fraction being formed at a given temperature.

### Conclusions

A new method to measure the amount of the solid forming in a solution using differential scanning calorimetry is proposed. Experimental solid fractions measured using this method for three systems present a very good agreement with data obtained by other techniques validating the proposed model. A graphical version of the calculation procedure is also presented. While a bit less accurate and of more limited applicability the graphical version is of much simpler use and is shown to give quick and reliable estimates for the solid fraction of many systems. Expressions to be used with other cases where no clear solvent exists or with multiple solvents are outside the scope of this article but can easily be derived using the approach presented in this work.

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### Nomenclatures

$C_p$	= heat capacity (J/g·K)
$h$	= enthalpy (J)
$h^E$	= excess enthalpy (J/g)
$h_m$	= melting enthalpy (J/g)
$m$	= mass (g)
$q$	= energy (J)
$T_c$	= cloud point temperature (K)
$T_m$	= melting point (K)
$W$	= mass fraction
$x$	= liquid phase molar fraction

### Greek letters

$\alpha^L$	= fraction of melted solute
$\alpha^S$	= fraction of crystallised solute

### Subscripts

$i$	= solute i
$liq$	= liquid
$m$	= melting
$slid$	= solid
$slt$	= solute
$solv$	= solvent

### Superscripts

$L$	= liquid
$slt$	= solute
$solv$	= solvent
$S$	= solid
$total$	= total

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