

A new method for measuring solid–liquid equilibrium phase diagrams using calorimetry

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Received 21 July 1997; accepted 27 January 1998

Abstract

A new experimental technique using calorimetric measurements to establish solid–liquid equilibrium (SLE) phase diagrams of binary systems of organic compounds with complete immiscibility in the solid phase is presented. Unlike some methods previously reported in the literature it is not based in the identification of the phase transition temperatures at different compositions of the mixture. Instead it measures the changes on the relative size of the liquid phase during the fusion of a mixture, that is later converted into a phase diagram using the lever rule. This technique, while somewhat less accurate than some processes based in the direct detection of phase transitions for measuring SLE phase diagrams, is much faster and presents an accuracy similar to other calorimetric techniques. It also makes possible to define the position of invariant points, such as the eutectic or peritectic, both in composition and temperature, or the composition of intermediate compounds, with a single calorimetric measurement. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Experimental technique; Solid–liquid equilibrium; Crystallisation; Phase diagram; Calorimetry; DSC

1. Introduction

The importance of knowing the phase diagram for a mixture in designing separation processes is well known, but the measurement of phase diagrams is costly and time consuming, restricting the amount of experimental information available. Crystallisation is a purification process particularly well suited for biological molecules for they tend to be heat sensitive, decomposing at high temperatures. Unfortunately, for complex molecules like biological products, the data are very scarce and the standard predictive models like UNIFAC proved to be very unreliable or of limited

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applicability [1]. Many different techniques have been presented in the literature for measuring solid–liquid equilibrium (SLE) phase diagrams in several different conditions [2], and among these some calorimetric methods such as differential scanning calorimetry (DSC) and differential thermal analysis (DTA). Some alternative processes, making use of the specificity of differential calorimetry, have been reported [3] but traditionally DSC is used in the same way as DTA to directly identify the temperatures of phase transition. The phase diagram is established by preparing a number of mixtures covering a part, or the entire composition range, and measuring the phase transitions for each mixture [4–7]. This is a very strong and flexible method for it allows the measurement of complex phase diagrams for binary or multicomponent systems with total or partial miscibility in any of the phases. For the systems presenting simple binary solid/liquid phase diagrams with complete immiscibility in the solid phase, which are about 1/3 of the systems with organic compounds [8], a much simpler approach can be used as presented here.

A whole range of compositions, theoretically the entire range between two invariant points, is measured in a single run making the phase diagram measurement procedure a lot faster and cheaper for it is time and material consuming. Instead of a direct measurement of phase transitions, the fraction of liquid forming during the melting of a sample is measured and then converted into phase boundaries using the lever rule. Recently, this idea has been applied to DTA measurements [9] for eutectic systems making use of several simplifications and some restrictive hypothesis. Here, a general thermodynamic derivation of the method will be presented showing that it can be applied to all systems showing no solubility in the solid phase, with or without the formation of intermediate compounds. This method has the limitations of the calorimetric techniques used, thus being a bit less accurate than other methods based on the visual detection of phase transitions [2,10]. However, its accuracy should not be much lower than that of other methods based in the interpretation of peaks issued from calorimetric measurements.

The thermodynamical background of this technique is developed and presented. The hypothesis used and the simplifications performed help to recognise the limits of validity and the reliability of the method. It is shown how to completely define the position of the invariant points, eutectic, peritectic and intermediate compounds, both in composition and temperature, with a single calorimetric measurement. A couple of experimental examples are presented showing the performance of the proposed technique in comparison with data obtained from alternative procedures [11]. The reader interested in this subject should also notice the work by Müller and Borchard [12] that was published during the revision of this work.

2. Thermodynamical background

2.1. Systems with an eutectic point and no intermediate compounds

As indicated before, this phase diagram measurement technique is not based on a direct measurement of the phase boundaries by means of some process of phase transition detection, but instead based on the measurement of the enthalpy variation upon heating, which allows the determination of the relative size of the liquid fraction, later converted into a phase diagram using the lever rule.

Consider a binary system presenting no solubility in the solid phase and complete miscibility in the liquid phase having the phase diagram sketched in Fig. 1. A mixture of composition W in component

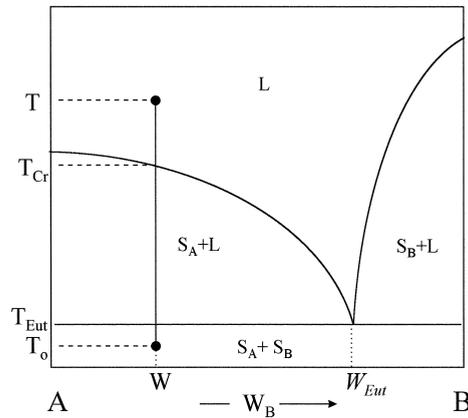


Fig. 1. Solid–liquid phase diagram with an eutectic point and complete immiscibility in the solid phase.

B, at a temperature T_0 inferior to T_{Eut} is heated until complete fusion. (Unless otherwise stated the compositions throughout this work always refer to component B.) The enthalpy variation with the temperature during the process is recorded and presented in Fig. 2.

The first step in the calorimetric analysis would be to check the position of the mixture relatively to the eutectic. The procedure to use for that purpose will be described later. For the moment it is assumed that $0 < W < W_{\text{Eut}}$. The enthalpy plot can be described by:

$$h(T) = h^a(T < T_{\text{Eut}}) + h^b(T = T_{\text{Eut}}) + h^c(T_{\text{Eut}} < T \leq T_{\text{Cr}}) + h^d(T_{\text{Cr}} < T) \quad (1)$$

with

$$h^a = m_{\text{A}}^{\text{total}} \int_{T_0}^T C_{\text{pA}}^{\text{S}} dT + m_{\text{B}}^{\text{total}} \int_{T_0}^T C_{\text{pB}}^{\text{S}} dT \quad (2)$$

$$h^b = m_{\text{A}}^{\text{LEut}} h_{\text{m}_A} \langle T_{\text{Eut}} \rangle + m_{\text{B}}^{\text{total}} h_{\text{m}_B} \langle T_{\text{Eut}} \rangle + (m_{\text{A}}^{\text{LEut}} + m_{\text{B}}^{\text{tot}}) h^{\text{E}} \quad (3)$$

$$h^c = m_{\text{B}}^{\text{total}} \int_{T_{\text{Eut}}}^T C_{\text{pB}}^{\text{L}} dT + \int_{T_{\text{Eut}}}^T m_{\text{A}}^{\text{S}} C_{\text{pA}}^{\text{S}} dT + \int_{T_{\text{Eut}}}^T m_{\text{A}}^{\text{L}} C_{\text{pA}}^{\text{L}} dT + \int_{T_{\text{Eut}}}^T h_{\text{m}_A} \frac{dm_{\text{A}}^{\text{L}}}{dT} dT + (m_{\text{B}}^{\text{total}} + m_{\text{A}}^{\text{L}} \langle T \rangle) h^{\text{E}} - (m_{\text{B}}^{\text{total}} + m_{\text{A}}^{\text{LEut}}) h^{\text{E}} \quad (4)$$

$$h^d = m_{\text{A}}^{\text{total}} \int_{T_{\text{Cr}}}^T C_{\text{pA}}^{\text{L}} dT + m_{\text{B}}^{\text{total}} \int_{T_{\text{Cr}}}^T C_{\text{pB}}^{\text{L}} dT \quad (5)$$

Where $P \langle T \rangle$ is the value of the property at temperature T . The meaning of the other symbols is the usual or is described in the nomenclature section. The effects due to the excess heat capacities in the liquid phase are neglected.

The goal is to measure:

$$\alpha_{\text{A}}^{\text{L}} = \frac{\int_{T_{\text{Eut}}}^T \frac{dm_{\text{A}}^{\text{L}}}{dT} dT}{\int_{T_{\text{Eut}}}^{T_{\text{Cr}}} \frac{dm_{\text{A}}^{\text{L}}}{dT} dT} = \frac{m_{\text{A}}^{\text{L}}}{m_{\text{A}}^{\text{total}}} \quad (6)$$

that is easily converted in phase boundaries using the lever rule.

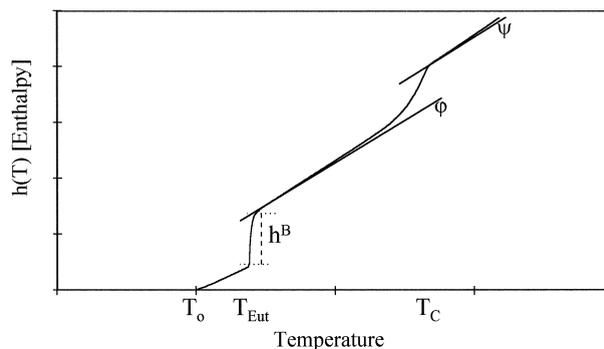


Fig. 2. Temperature dependence of the enthalpy of the mixture which phase diagram is shown in Fig. 1.

The fusion of component A occurs in two steps: a portion melts at the eutectic point, m_A^{LEut} , and another between T_{Eut} and T_C , $m_A^{\text{L}^*}(T)$. Two accessory liquid fractions will thus be defined:

$$\alpha_A^{\text{LEut}} = \frac{m_A^{\text{LEut}}}{m_A^{\text{total}}} \quad (7)$$

$$\alpha_A^{\text{L}^*} = \frac{m_A^{\text{L}^*}}{m_A^{\text{SEut}}} \quad (8)$$

where $m_A^{\text{SEut}} = m_A^{\text{total}} - m_A^{\text{LEut}}$. The relation between these three liquid fractions is simply given by:

$$\alpha_A^{\text{L}} = \alpha_A^{\text{LEut}} + \alpha_A^{\text{L}^*} (1 - \alpha_A^{\text{LEut}}) \quad (9)$$

The estimation of $\alpha_A^{\text{L}^*}$ is first considered. Using calorimetry only enthalpic rather than mass variations can be accounted for. What can be measured is the ratio between the energy required to the fusion of the amount of component A that melts between the eutectic point and temperature T , $m_A^{\text{L}^*} \langle T \rangle$, and the energy required to complete fusion of the fraction of component A that remains solid at the eutectic, $m_A^{\text{SEut}} = m_A^{\text{L}^*} \langle T_{\text{Cr}} \rangle$:

$$\alpha_A^{\text{L}^*} = \frac{\int_{T_{\text{Eut}}}^T h_{m_A} \frac{dm_A^{\text{L}}}{dT} dT}{\int_{T_{\text{Eut}}}^{T_{\text{Cr}}} h_{m_A} \frac{dm_A^{\text{L}}}{dT} dT} = \frac{q \langle T \rangle}{q_{\text{total}}} \quad (10)$$

The melting enthalpies at a generic temperature T are related with melting enthalpies at the melting temperature by:

$$h_m(T) = h_m \langle T_m \rangle + \int_{T_m}^T (C_p^{\text{S}} - C_p^{\text{L}}) dT \quad (11)$$

but since the difference of heat capacities between the two phases is much smaller than the enthalpies of melting it can be assumed that the melting enthalpies are, to a fair extent, temperature independent, therefore $\alpha_A^{\text{L}^*}$ can be considered equivalent to $\alpha_A^{\text{L}^*}$.

Unfortunately, it is not possible to access directly by a calorimetric measurement the energies defined as $q\langle T \rangle$ and q_{total} . Together with 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 measured. It is thus necessary to isolate the energy used for melting the solute from the other two.

Eq. (8) can thus be related to the measured enthalpy variations by:

$$\alpha_{\text{A}}^{\text{L}*} = \alpha_{\text{A}}^{\text{L}*} = \frac{h(T) - I(T)}{h(T_{\text{Cr}}) - I(T_{\text{Cr}})} \quad (12)$$

where $I(T)$ is:

$$I(T) = h\langle T_{\text{Eut}} \rangle + m_{\text{B}}^{\text{total}} \int_{T_{\text{Eut}}}^T C_{\text{pB}}^{\text{L}} dT + \int_{T_{\text{Eut}}}^T m_{\text{A}}^{\text{S}} C_{\text{pA}}^{\text{S}} dT + \int_{T_{\text{Eut}}}^T m_{\text{A}}^{\text{L}} C_{\text{pA}}^{\text{L}} dT + (m_{\text{B}}^{\text{total}} + m_{\text{A}}^{\text{L}}\langle T \rangle) h^{\text{E}} \quad (13)$$

The I represents the energy required to heat the mixture from the eutectic point to temperature T and the heat effects associated to the mixing of solute and solvent in the liquid phase. It cannot be calculated because even if the composition of the solution, the excess enthalpy and the heat capacities were known, and they seldom are, the masses of solute in the solid and liquid phases at each temperature would still be unknown. To estimate I from the measured data another approach will be followed.

A straight line, φ , tangent to the curve just above the eutectic point is drawn. It describes the energy required to heat the mixture present at the eutectic point:

$$\varphi(T) = h\langle T_{\text{Eut}} \rangle + (m_{\text{B}}^{\text{total}} C_{\text{pB}}^{\text{L}}\langle T_{\text{Eut}} \rangle + m_{\text{A}}^{\text{SEut}} C_{\text{pA}}^{\text{S}}\langle T_{\text{Eut}} \rangle + m_{\text{A}}^{\text{LEut}} C_{\text{pA}}^{\text{L}}\langle T_{\text{Eut}} \rangle)(T - T_{\text{Eut}}) \quad (14)$$

Another straight line, ψ , is drawn just above the temperature of disappearing of the last crystal, the cloud point temperature, T_{Cr} . It represents the energy used to heat the solution above the T_{Cr} :

$$\psi(T) = h\langle T_{\text{Cr}} \rangle + (m_{\text{B}}^{\text{total}} C_{\text{pB}}^{\text{L}}\langle T_{\text{Cr}} \rangle + m_{\text{A}}^{\text{total}} C_{\text{pA}}^{\text{L}}\langle T_{\text{Cr}} \rangle)(T - T_{\text{Cr}}) \quad (15)$$

If the heat capacities are assumed to be approximately temperature independent it is possible to show that:

$$\frac{dI}{dT} = \frac{d\varphi}{dT} + \alpha_{\text{A}}^{\text{L}*} \left(\frac{d\psi}{dT} - \frac{d\varphi}{dT} \right) + \frac{1}{\alpha_{\text{A}}^{\text{L}*}} \frac{d\alpha_{\text{A}}^{\text{L}*}}{dT} h^{\text{E}} m_{\text{B}}^{\text{total}} \quad (16)$$

For athermal solutions or solutions with a low heat of mixing, the last term of dI/dT can be neglected without a significant effect on $\alpha_{\text{A}}^{\text{L}*}$. For mixtures with higher excess enthalpies this term is also usually negligible because h^{E} and $(1/\alpha_{\text{A}}^{\text{L}*} \times d\alpha_{\text{A}}^{\text{L}*}/dT)$ present opposite variations with the temperature and tend to cancel each other.

If the last term is neglected, knowing that $I\langle T_{\text{Eut}} \rangle = h\langle T_{\text{Eut}} \rangle$ the numerical integration of dI/dT can be readily performed and with a simple iterative procedure the value of $\alpha_{\text{A}}^{\text{L}*}$ calculated. The assumption of temperature independent heat capacities made above affects only the term $(d\varphi/dT - d\psi/dT)$. However, the slopes of the two straight lines are usually not very different. Moreover, $\alpha_{\text{A}}^{\text{L}*}$ ranges from 0 to 1 further reducing its effect. Normally, assuming temperature independent heat capacities does not affect the value of dI/dT by more than 2% and influences the estimation of $\alpha_{\text{A}}^{\text{L}*}$ by less than 0.1% for $\alpha_{\text{A}}^{\text{L}*} > 0.01$.

When the slopes of φ and ψ do not differ more than 20% making $I = \varphi$ would introduce a relative error inferior to 2.5% in α_A^{L*} for $\alpha_A^{L*} > 0.01$ very much simplifying the calculation procedure. Although this simplification may not always be acceptable, it always provides a good starting point for the iteration of α_A^{L*} .

With α_A^{L*} known, the next step is to calculate α_A^{LEut} to obtain α_A^L from Eq. (9). The definition of a total liquid fraction at the eutectic temperature, α_{total}^{LEut} :

$$\alpha_{total}^{LEut} = \frac{m_A^{LEut} + m_B^{total}}{m_A^{total} + m_B^{total}} \quad (17)$$

is helpful because this quantity is related with α_A^{LEut} by:

$$\alpha_A^{LEut} = \frac{\alpha_{total}^{LEut} - W}{1 - W} \quad (18)$$

and from Eqs. (3) and (17) it is possible to show that it can be estimated from the measured quantities as:

$$\alpha_{total}^{LEut} = \frac{\frac{h^b}{m_{total}} - W(h_{m_B} - h_{m_A})}{h_{m_A} + h^E} \quad (19)$$

where m_{total} is the mass of the sample being analysed and the heats of fusion are those at the eutectic temperature. Since normally $h_{m_A} \gg h^E$ the total liquid fraction at the eutectic point can immediately be calculated and from it α_A^L . But α_{total}^{LEut} presents also another interest. If the lever rule is applied to the eutectic point, using Eq. (17) and some algebraic manipulation, it is possible to relate α_{total}^{LEut} to the composition of the eutectic point:

$$W_{Eut} = \frac{W}{\alpha_{total}^{LEut}} \quad (20)$$

This means that with a single calorimetric measurement the eutectic point is completely defined, its temperature being obtained from the jump on the curve of Fig. 2 and the composition from the total liquid fraction at the eutectic point, α_{total}^{LEut} , as given by Eq. (20).

Please note that these equations like all the others presented before are valid only for $0 < W < W_{Eut}$. For this reason before making the analysis of a calorimetric measurement the eutectic point must be located to know how to perform the analysis correctly. This is done using the Eqs. (19) and (20) above, together with the following couple of equations valid for $W_{Eut} < W < 1$:

$$\alpha_{total}^{LEut} = \frac{\frac{h^b}{m_{total}} + (1 - W)(h_{m_B} - h_{m_A})}{h_{m_B} + h^E} \quad (21)$$

and

$$W_{Eut} = \frac{(1 - W)}{\alpha_{total}^{LEut}} \quad (22)$$

Using these four equations it is possible to calculate the composition at the eutectic point since only one of the couples will produce a physically meaningful result. The placement of the mixture relatively to the eutectic point indicates the procedure to be used in the estimation of α_A^L . If $W_{\text{Eut}} < W < 1$ the method is by all means similar to that described before but the indexes referring to the compounds have to be changed.

The phase boundaries are obtained with no difficulties from α_A^L using the lever rule. The relation between the composition at the phase boundaries, W^L , and the liquid fraction, α_A^L , is given by:

$$W^L = \frac{W}{W + (1 - W)\alpha_A^L} \quad \text{for } 0 < W < W_{\text{Eut}} \quad (23)$$

$$W^L = \frac{\alpha_B^L W}{1 + W(\alpha_B^L - 1)} \quad \text{for } W_{\text{Eut}} < W < 1 \quad (24)$$

2.2. System with an intermediate compound with a congruent melting point

Systems that present the formation of an intermediate compound with a congruent melting point can also be treated with the formalism described. Consider the binary system with the phase diagram sketched in Fig. 3. Beside the pure compounds it presents three other invariant points, W_{E1} , W_{E2} and W_{AB} . This last is the composition of the A_xB_y intermediate compound from now on to be referred as AB. Two mixtures of compositions W_i and W_{ii} in component B are to be used in the measurement covering the composition range $0 < W < W_{AB}$ of the phase diagram. The range $W_{AB} < W < 1$ is treated identically.

Again, as it was done before, the melting of the samples is treated in two steps: the melting at the eutectic point and the melting at temperatures above the eutectic. The estimation of α_A^{L*} is identical to the preceding case. The difference lies in the estimation of $\alpha_{\text{total}}^{\text{LEut}}$. This is not as simple as before due to the presence of the intermediate compound AB. Two measures, at W_i and W_{ii} are required to provide information simultaneously on W_{E1} , W_{AB} .

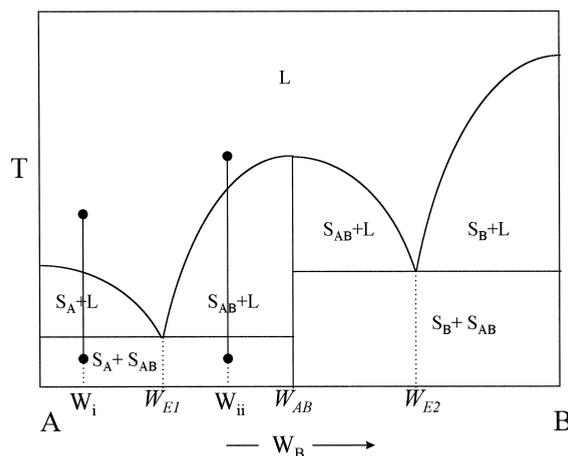


Fig. 3. Solid–liquid phase diagram for a system with an intermediate compound A_xB_y stable up to the melting point.

For the measurement at W_i , the total liquid fraction at the eutectic is obtained from the measured enthalpy variation as:

$$\alpha_{\text{total}}^{\text{LEut}} = \frac{\frac{h^b}{m_{\text{total}}} + \frac{W}{W_{\text{AB}}}(h_{m_{\text{AB}}} - h_{m_{\text{A}}})}{h_{m_{\text{A}}} + h^E} \quad (25)$$

being related with the eutectic composition by:

$$W_{\text{Eut}} = \frac{W}{\alpha_{\text{total}}^{\text{LEut}}} \quad (26)$$

For the measurement at W_{ii} , the total liquid fraction at the eutectic is given by:

$$\alpha_{\text{total}}^{\text{LEut}} = \frac{\frac{h^b}{m_{\text{total}}} + \left(1 - \frac{W}{W_{\text{AB}}}\right)(h_{m_{\text{A}}} - h_{m_{\text{AB}}})}{h_{m_{\text{AB}}} + h^E} \quad (27)$$

and the composition of the intermediate compound is obtained from the lever rule as:

$$W_{\text{AB}} = W + \frac{\alpha_{\text{total}}^{\text{LEut}}}{1 - \alpha_{\text{total}}^{\text{LEut}}}(W - W^E) \quad (28)$$

Using the experimental data from the two measurements and the Eqs. (25)–(28) W_{AB} and W_{Ei} are obtained. Since W_{AB} cannot be any arbitrary composition because x and y have to be integers, its value will be correctly known reducing the uncertainties associated to the experimental measurements and the calculation procedure.

The relation between $\alpha_{\text{total}}^{\text{LEut}}$ and $\alpha_{\text{AB}}^{\text{LEut}}$ for the sample at W_i is the same presented before in Eq. (18). For the sample at W_{ii} is somewhat different due to the presence of compound AB:

$$\alpha_{\text{AB}}^{\text{LEut}} = W_{\text{AB}} \left(\frac{\alpha_{\text{total}}^{\text{LEut}} - (1 - W)}{W} + \frac{1 - W_{\text{AB}}}{W_{\text{AB}}} \right) \quad (29)$$

being the relation between the different liquid fractions:

$$\alpha_{\text{AB}}^{\text{L}} = \alpha_{\text{AB}}^{\text{LEut}} + \alpha_{\text{AB}}^{\text{L}*} (1 - \alpha_{\text{AB}}^{\text{LEut}}) \quad (30)$$

2.3. System with an intermediate compound with an incongruent melting point. Peritectic point

The case of a system with a peritectic point is discussed now. The phase diagram for such a system is presented in Fig. 4 [2]. The region $0 < W < W_{\text{Per}}$ presents no differences to the case studied in the previous section being possible from measurements at W_i and W_{ii} to measure that region of the phase diagram and define also the composition of W_{AB} . Another measurement at W_{iii} will provide the description of the remaining portion of the phase diagram and the composition of the peritectic point W_{Per} .

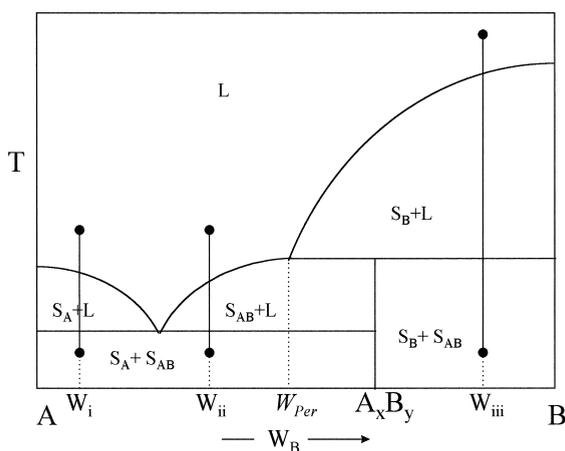


Fig. 4. Solid–liquid phase diagram for a system with a peritectic point.

Again the fusion is to be split into two parts, a fusion at the peritectic point, α_B^{LPer} , and the remaining above this temperature, $\alpha_B^{\text{L}*}$, being the liquid fractions related with the total liquid fraction, α_B^{L} , by:

$$\alpha_B^{\text{L}} = \alpha_B^{\text{LPer}} + \alpha_B^{\text{L}*} (1 - \alpha_B^{\text{LPer}}) \quad (31)$$

As before the estimation of $\alpha_B^{\text{L}*}$ is identical to what was done for the simple eutectic system, and α_B^{LPer} is related to the total liquid fraction at the peritectic point, $\alpha_{\text{total}}^{\text{LPer}}$, by:

$$\alpha_B^{\text{LPer}} = \frac{\alpha_{\text{total}}^{\text{LPer}} - (1 - W)}{W} \quad (32)$$

This liquid fraction is obtained from the enthalpy variation at the eutectic point, h^b , and the melting enthalpies of the pure compounds according to:

$$\alpha_{\text{total}}^{\text{LPer}} = \frac{\frac{h^b}{m_{\text{total}}} - \left(\frac{1 - W}{1 - W_{\text{AB}}} \right) (h_{m_{\text{AB}}} - h_{m_{\text{B}}})}{h_{m_{\text{B}}} + h^E} \quad (33)$$

from where the composition of the peritectic point, W_{Per} , is obtained:

$$W_{\text{Per}} = 1 - \frac{1 - W}{\alpha_{\text{total}}^{\text{LPer}}} \quad (34)$$

This procedure allows the conversion of calorimetric measurements into SLE phase diagrams. It shows that a lot more of information can be drawn from the calorimetric results than just the transition temperatures and/or the enthalpies of phase transition. Whenever a system is suspected to be a simple eutectic, be it from calorimetric experiments or because the phase diagrams for compounds in the same family present a simple eutectic, and this is a very common situation among organic compounds where more than 25% of the solid/liquid phase diagrams are of this kind [8], the phase diagram can be immediately established with a couple of measurements that should not take longer than a few

Table 1

Enthalpy variation for a sample of $n\text{-C}_{19}\text{H}_{40}$ /ethylbenzene ($W_{n\text{-C}_{19}\text{H}_{40}} = 0.2247$)

T (K)	h (mJ)						
158.73	0	196.76	7102.7	234.90	8643.1	272.61	11,828
159.59	0.679	197.63	7136.4	235.77	8682.0	273.44	12,022
160.46	2.031	198.50	7170.0	236.63	8721.4	274.27	12,230
161.33	3.895	199.37	7203.2	237.50	8761.3	275.08	12,454
162.19	5.608	200.23	7236.5	238.36	8801.8	275.90	12,696
163.06	7.163	201.10	7269.8	239.23	8842.6	276.70	12,960
163.93	9.316	201.97	7303.1	240.10	8883.6	277.50	13,246
164.79	11.06	202.83	7336.3	240.96	8924.9	278.30	13,555
165.66	12.98	203.70	7369.6	241.83	8966.6	279.09	13,889
166.52	15.64	204.57	7402.9	242.70	9008.9	279.89	14,247
167.39	17.83	205.43	7436.1	243.56	9051.8	280.69	14,628
168.25	20.49	206.30	7469.4	244.43	9095.2	281.54	15,023
169.12	24.06	207.17	7502.7	245.30	9139.0	282.50	15,402
169.99	27.29	208.03	7536.0	246.16	9183.8	283.68	15,708
170.85	30.06	208.90	7569.2	247.03	9229.5	284.90	15,901
171.72	32.49	209.77	7602.5	247.90	9276.0	285.93	16,009
172.59	34.89	210.63	7635.8	248.76	9323.1	286.86	16,081
173.45	38.23	211.50	7669.0	249.63	9371.0	287.75	16,139
174.32	42.73	212.37	7702.3	250.50	9419.8	288.62	16,192
175.19	47.04	213.23	7735.6	251.36	9469.5	289.49	16,244
176.05	50.94	214.10	7768.9	252.23	9520.7	290.36	16,296
176.92	55.32	214.97	7802.1	253.06	9573.7	291.23	16,347
177.78	60.99	215.83	7836.0	253.93	9628.7	292.09	16,399
178.65	67.70	216.70	7870.4	254.80	9685.3	292.96	16,451
179.51	75.36	217.57	7904.5	255.65	9743.2	293.83	16,503
180.36	85.81	218.43	7938.9	256.51	9803.3	294.69	16,556
181.20	102.43	219.30	7974.2	257.37	9866.3	295.56	16,611
182.00	134.25	220.17	8009.9	258.23	9932.0	296.43	16,665
182.62	216.92	221.03	8045.6	259.09	10,000	297.29	16,719
182.93	426.32	221.90	8081.6	259.94	10,071	298.16	16,774
183.08	831.10	222.77	8117.5	260.80	10,146	299.03	16,829
183.22	1452.9	223.63	8153.9	261.66	10,224	299.89	16,884
183.47	2273.3	224.50	8190.6	262.51	10,306	300.76	16,939
183.89	3249.5	225.37	8227.2	263.37	10,393	301.63	16,994
184.59	4312.6	226.23	8264.1	264.22	10,484	302.49	17,049
185.68	5358.0	227.10	8300.8	265.07	10,581	303.36	17,105
187.64	6186.6	227.97	8337.8	265.92	10,684	304.22	17,161
189.92	6636.3	228.83	8374.9	266.76	10,795	305.09	17,216
191.29	6815.7	229.70	8412.2	267.61	10,913	305.96	17,272
192.33	6901.2	230.57	8449.9	268.44	11,038	306.82	17,330
193.26	6954.3	231.43	8487.7	269.29	11,173	307.69	17,386
194.14	6996.1	232.30	8525.8	270.12	11,319	308.56	17,444
195.02	7033.4	233.17	8564.4	270.95	11,476	309.42	17,502
195.89	7068.6	234.03	8603.8	271.78	11,646	310.29	17,560

Table 2

Enthalpy variation for a sample of $n\text{-C}_{22}\text{H}_{46}$ /ethylbenzene ($W_{n\text{-C}_{22}\text{H}_{46}} = 0.2144$)

T (K)	h (mJ)								
153.15	0	186.15	6527.4	219.15	9758.7	252.15	12,828	285.15	16,913
153.90	50.841	186.90	6644.0	219.90	9827.9	252.90	12,900	285.90	17,089
154.65	99.422	187.65	6755.7	220.65	9898.2	253.65	12,972	286.65	17,278
155.40	147.44	188.40	6859.7	221.40	9967.0	254.40	13,043	287.40	17,477
156.15	195.78	189.15	6955.2	222.15	10,038	255.15	13,115	288.15	17,688
156.90	243.63	189.90	7037.8	222.90	10,107	255.90	13,187	288.90	17,915
157.65	291.38	190.65	7110.3	223.65	10,175	256.65	13,260	289.65	18,160
158.40	340.19	191.40	7182.2	224.40	10,244	257.40	13,332	290.40	18,420
159.15	389.60	192.15	7253.7	225.15	10,314	258.15	13,405	291.15	18,704
159.90	439.99	192.90	7324.1	225.90	10,384	258.90	13,478	291.90	19,006
160.65	490.42	193.65	7393.2	226.65	10,453	259.65	13,551	292.65	19,329
161.40	540.54	194.40	7461.3	227.40	10,522	260.40	13,626	293.40	19,632
162.15	591.26	195.15	7531.7	228.15	10,592	261.15	13,702	294.15	19,888
162.90	642.10	195.90	7601.2	228.90	10,661	261.90	13,778	294.90	20,035
163.65	693.09	196.65	7670.9	229.65	10,730	262.65	13,854	295.65	20,138
164.40	742.39	197.40	7739.9	230.40	10,800	263.40	13,931	296.40	20,225
165.15	792.39	198.15	7809.5	231.15	10,871	264.15	14,008	297.15	20,304
165.90	842.65	198.90	7880.0	231.90	10,941	264.90	14,086	297.90	20,379
166.65	893.96	199.65	7948.6	232.65	11,010	265.65	14,165	298.65	20,453
167.40	945.38	200.40	8016.4	233.40	11,080	266.40	14,244	299.40	20,529
168.15	996.39	201.15	8086.3	234.15	11,151	267.15	14,322	300.15	20,605
168.90	1047.4	201.90	8155.7	234.90	11,220	267.90	14,404	300.90	20,683
169.65	1097.7	202.65	8225.4	235.65	11,291	268.65	14,486	301.65	20,757
170.40	1149.5	203.40	8295.1	236.40	11,360	269.40	14,568	302.40	20,833
171.15	1199.7	204.15	8364.7	237.15	11,432	270.15	14,652	303.15	20,908
171.90	1252.0	204.90	8432.6	237.90	11,500	270.90	14,739	303.90	20,983
172.65	1303.5	205.65	8501.8	238.65	11,569	271.65	14,826	304.65	21,058
173.40	1354.0	206.40	8571.1	239.40	11,638	272.40	14,914	305.40	21,133
174.15	1403.2	207.15	8639.7	240.15	11,707	273.15	15,003	306.15	21,207
174.90	1453.4	207.90	8709.6	240.90	11,776	273.90	15,094	306.90	21,283
175.65	1503.4	208.65	8779.2	241.65	11,847	274.65	15,189	307.65	21,358
176.40	1553.4	209.40	8849.3	242.40	11,916	275.40	15,284	308.40	21,434
177.15	1604.1	210.15	8921.5	243.15	11,985	276.15	15,381	309.15	21,510
177.90	1653.5	210.90	8990.6	243.90	12,054	276.90	15,481	309.90	21,586
178.65	1704.7	211.65	9060.1	244.65	12,125	277.65	15,585	310.65	21,663
179.40	1756.8	212.40	9129.8	245.40	12,195	278.40	15,692	311.40	21,738
180.15	1808.8	213.15	9200.0	246.15	12,265	279.15	15,802	312.15	21,814
180.90	1862.9	213.90	9269.1	246.90	12,336	279.90	15,919	312.90	21,890
181.65	1920.8	214.65	9339.1	247.65	12,406	280.65	16,041	313.65	21,967
182.40	2000.7	215.40	9408.8	248.40	12,477	281.40	16,170	314.40	22,043
183.15	4322.8	216.15	9477.4	249.15	12,546	282.15	16,302	315.15	22,119
183.90	5658.0	216.90	9549.0	249.90	12,616	282.90	16,442	315.90	22,195
184.65	6195.6	217.65	9618.7	250.65	12,686	283.65	16,589	316.65	22,272
185.40	6399.8	218.40	9689.2	251.40	12,757	284.40	16,746	317.40	22,349

hours or use more than some milligrams of compound. If an intermediate compound exists the procedure becomes somewhat more complex, more measurements are needed as well as the enthalpy of melting of this new compound. Yet the same approach is applicable in the search for the invariant points of the phase diagrams and to establish the phase boundaries. This technique can also be used as a complement to some other phase diagram measurement techniques helping to establish the coherence of the measurements, identify and eliminate systematic deviations, or to speed up these measurements by identifying the composition of the invariant points, such as the eutectics, peritectics, or the intermediate compounds compositions. The presence of solid phase transitions is not a limitation to the applicability of this technique that can easily be extended to pseudo-binaries where the solubility of a solute in a mixture of solvents is to be studied.

3. Experimental measurements

To test the performance of the proposed technique, two solutions, one of nonadecane and the other of docosane (Fluka with a purity of at least 99%) in ethylbenzene (Aldrich, 99.8%) were prepared and their phase diagrams measured. Aluminium pans of 150 μl were filled up to 2/3 with the solutions and analysed in a Mettler TA 3000 DSC. The calorimeter 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 heated from 150 K up to 320 K at a rate of 1 K/min. The use of a low heating rate is very important to assure an equilibrium state during the heating. The enthalpy changes were registered every 0.75 K between the starting and final temperatures. They are presented in Tables 1 and 2 and were treated according to the procedure proposed in the previous section.

The analysis of the position of the eutectic point indicates that $W_{\text{EB Eut}} > 0.99$. For calculation purposes it was considered that $W_{\text{EB}} = 1$. The measured phase diagrams are shown in Fig. 5. Data for the system nonadecane/ethylbenzene were previously unavailable in the literature, for the system docosane/ethylbenzene a comparison with data by Ghogomu et al. [11] is presented. There is a very

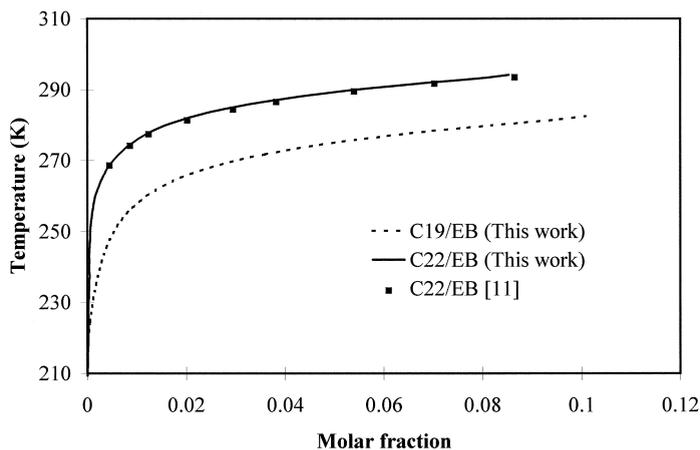


Fig. 5. Solid–liquid phase diagrams for nonadecane/ethylbenzene and docosane/ethylbenzene measured by DSC using the proposed technique.

good agreement between the two sets of data showing the potential of the proposed technique in solid/liquid phase diagram measurements.

4. Conclusions

A new technique using calorimetry for measuring solid/liquid phase diagrams of binary mixtures completely immiscible in the solid phase, with or without the formation of intermediate compounds, and to locate the invariant points, is presented.

Unlike other methods for phase diagram measurement reported in the literature, this method does not perform a direct determination of the phase transition temperatures. Instead it measures the fraction of melted solution, that converts into a phase diagram using the lever rule. While being of a more limited applicability and somewhat lower accuracy than other methods currently used, the proposed technique is much faster and cheaper since a single measurement is enough to define the phase diagram in the region between two invariant points. It can either be used to directly establish a phase diagram or as a complement to any other phase diagram measurement technique helping to establish the coherence of the measurements, identify and eliminate systematic deviations, or to speed up these measurements by identifying the composition of the invariant points, such as the eutectics, peritectics, or the intermediate compounds compositions.

It is shown that a lot more of information can be drawn from the calorimetric results than just the transition temperatures and/or the enthalpies of phase transition. Measurements using this new technique show a very good agreement with data by other authors showing the potentialities of the proposed technique.

5. Nomenclature

C_p	heat capacity
h	enthalpy
h_E	excess enthalpy
h_m	melting enthalpy
m	mass
q	energy
T_c	cloud point temperature
T_{Eut}	eutectic point temperature
T_m	melting point
T_0	starting temperature
V	molar volume
W	mass fraction

Greek letters

α^L	fraction of component melted
α^S	fraction of component crystallised

φ	straight line defined in Eq. (14)
ψ	straight line defined in Eq. (15)

Subscripts and superscripts

A	component A
B	component B
AB	component A _x B _y
Eut	relative to the eutectic point
liq	liquid
L	liquid
m	melting
Per	relative to the peritectic point
S	solid
total	total

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