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Enthalpies of non-isothermal phase transitions in binary systems

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Abstract

Two kinds of non-isothermal phase transitions in binary systems are considered: transformation of one phase into another and transition from two phases to one phase following an isothermal three-phase reaction (eutectic, peritectic or incongruent melting). The enthalpy of these transitions is defined on the basis of the equation for the heat capacity of a biphasic binary system. It is concluded that for most one-phase–one-phase transformations, the straightforward procedure of drawing a baseline can be applied. For two-phase–one-phase transitions following a eutectic reaction, however, the area corresponding to the transition enthalpy has an unexpected shape.

DSC data on heat capacities and transition enthalpies are presented for the lamellar/liquid and lamellar + crystals $\rightleftharpoons$ liquid transitions in aqueous solutions of the non-ionic surfactants decyldimethylphosphine oxide and dodecyldimethylphosphine oxide.

INTRODUCTION

Phase transitions in two-component systems display greater variety and complexity than those in pure substances. At fixed pressure, a phase transition in a binary system can be isothermal (invariant—the phases coexist only at a certain temperature, and a heterogeneous system has no degrees of freedom) or non-isothermal (univariant—the phases coexist in some temperature interval, and a biphasic system has one degree of freedom) [1, 2].

A DSC or adiabatic calorimetric study of a binary system usually yields the enthalpies of the phase transformations; for example, for metal alloys [3], mixtures containing salts [4–6], hydrocarbons [7], anhydrous surfactants [8], organic substances [9–13], and thermotropic [14, 15] and lyotropic [16–20] liquid crystals, etc. In many cases, the phase transitions for which the enthalpies are reported are actually non-isothermal. However, there is no generally accepted thermodynamic definition for the enthalpy of a non-isothermal phase transition in a binary system.

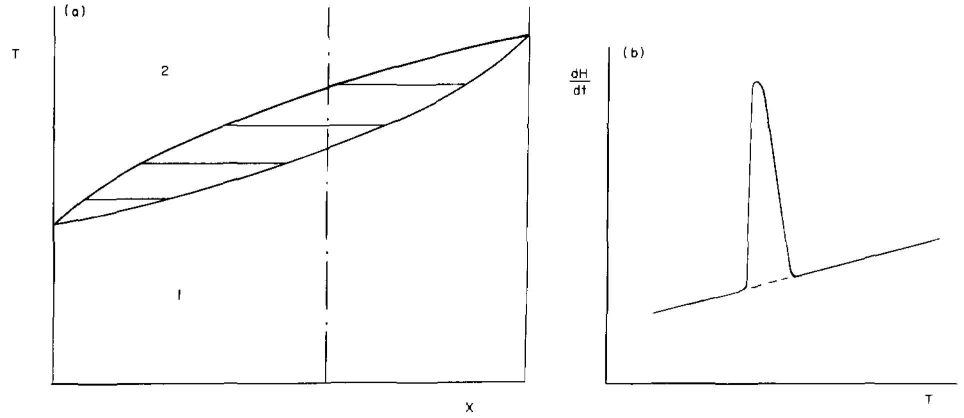

Fig. 1. Univariant transformation of phase 1 into phase 2: (a) phase diagram; (b) DSC curve.

In calorimetric studies, the problem of drawing a baseline in order to determine the area of a peak always arises because it affects the quality and reproducibility of the data. This problem is discussed in the literature, but the focus of attention is usually placed on isothermal transitions in pure substances; for example in refs. 21–24. These results can be readily applied to invariant transformations (such as congruent melting), but not to non-isothermal phase transitions in binary systems. Binary mixtures are included in the studies reported in refs. 25 and 26; however, the specific features of transitions in two-component systems are not taken into account.

In a phase diagram of a binary system, transformations of one phase into another over a certain temperature range may be observed, (see, for example, Fig. 1(a)). Another example of a non-isothermal phase transition is that preceding or following an isothermal phase reaction (eutectic, peritectic or incongruent melting). An example of a phase diagram with a eutectic phase transition is given in Fig. 2(a). The number of phases observed as the temperature is raised, for a mixture of a certain composition, is one, two and one for the former case and two, three, two and one for the latter.

Transition enthalpies are reported in the literature for non-isothermal phase processes of both types: for one-phase–one-phase transitions, for example, refs. 5, 9, 12, 13; for two-phase–one-phase transitions following a eutectic phase reaction, for example, refs. 10, 12, 13, 27, 28. In ref. 9, the enthalpy of fusion for benzene–thiophene mixtures was measured by adiabatic calorimetry; the transition occurs over an approximate temperature range (ΔT) of 10 K. In ref. 5, the results for the K_2CO_3–$BacO_3$ system are reported; the enthalpies for solid–liquid transitions over broad temperature intervals ($\Delta T \approx 70$ K) are given.

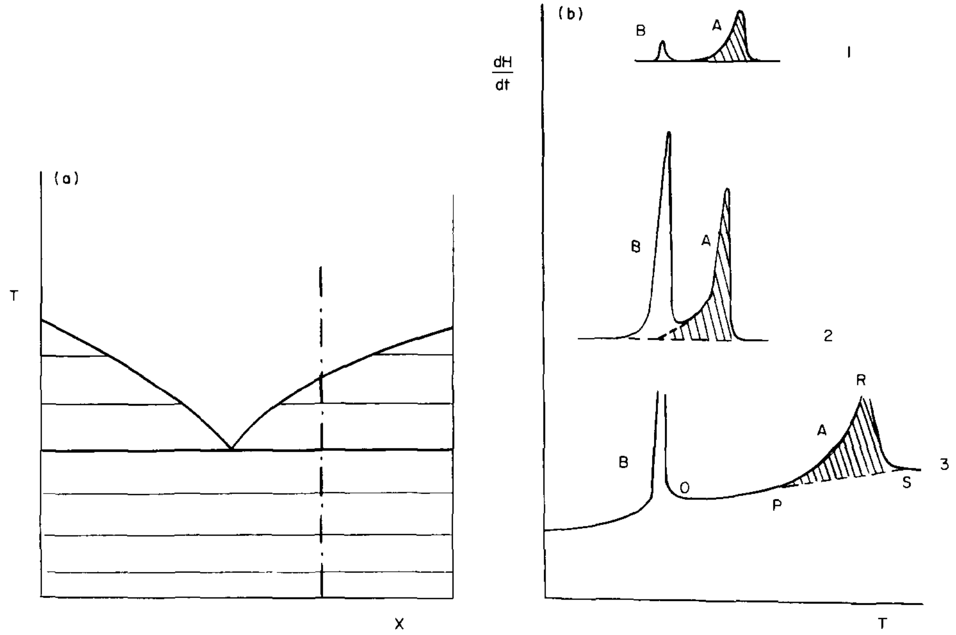

Fig. 2. Univariant transformation following a eutectic phase reaction: (a) phase diagram; (b) DSC curves. Schematic presentation of the evaluation of the area of peak A (indicated by shading): 1, ref. 27; 2, ref. 17; 3, ref. 10.

The case of one-phase–one-phase transformations is relatively simple. If the post-transition baseline is regarded as a continuation of the pre-transition baseline, see Fig. 1(b), i.e. if the heat capacity C_p of the system after the transition depends upon temperature in the same way as before, it seems natural to join the initial and final points of the peak with a straight line and to determine the heat of transition from the area under the DSC curve using this baseline. In general, in these cases authors do not discuss the question of drawing a baseline; they most probably draw a straight line as described above. The question becomes less trivial if there is a shift and/or a different slope in the heat capacity of a system after the transition. In a study of the NH_4F–water system using adiabatic calorimetry [6], the enthalpy of a non-isothermal solid–liquid transition was found by extrapolating the heat capacity curves for the solid and liquid phases to the temperature at which the apparent heat capacity was a maximum.

In the case of a two-phase–one-phase transition (following an isothermal phase reaction), various definitions for the enthalpy of the system can be encountered in the literature, because almost every author draws a baseline in his own way. Figure 2(b) shows different ways of drawing a baseline; the evaluation of peak A area is indicated by shading. Peak B corresponds to the eutectic phase transformation, and peak A to the subsequent non-isothermal two-phase–one-phase transition. The enthalpy definitions presented in curves 1, 2 and 3 can be encountered in refs. 27, 17 and 10, respectively. In ref. 10, the peak area PRS (curve 3) is ascribed to the transition enthalpy. The first peak is considered to correspond to the solid–solid transition and the second to melting. This implies that the fragment OP refers to the C_p of a single phase. However, analysis of data given in ref. 10 shows that peak B is observed at the same temperature for the four studied compositions, which undoubtly indicates that peak B refers to an isothermal three-phase reaction. Additional data are needed to determine whether it is eutectic, peritectic or incongruent melting; here it is assumed to be eutectic. It must be concluded that the section of the curve OPR actually corresponds to the heat capacity of the biphasic system. In ref. 4 (in a similar situation), the enthalpies were calculated from the area enclosed by both peaks, because it was not possible to separate them in the DSC curves.

Thus, it is necessary to discuss what thermodynamic value is defined as the enthalpy of a univariant phase transition in a binary mixture. In this paper a definition will be applied, based on a rigorous equation for the heat capacity of a biphasic system. Both cases, i.e. with the numbers of phases being one, two, one and two, three, two, one will be considered. In the theoretical section below, it will be assumed that we are able to measure accurately the heat capacities of the mixtures; any consideration of the kinetics of heat flow in a calorimetric experiment will be avoided.

Experimental illustrations include heat capacity and enthalpy data for aqueous solutions of the non-ionic surfactants decyldimethylphosphine oxide and dodecyldimethylphosphine oxide. In these systems, crystals, isotropic liquid and lyotropic liquid crystalline phases are observed [19, 29]. The specific features of the liquid crystals are not considered in this work the systems merely being examples of binary systems with invariant and univariant phase transitions.

THEORY

Transformation of one phase into another

Let us consider three fragments of a phase diagram of a binary system (Fig. 3(a)–(c)). At $x = x_a$ (Fig. 3(a)) a transition from phase 1 to phase 2 takes place isothermally; the transition temperature is the maximum and point P may be called an azeotrope point. (In translation, "azeotrope" means "boiling without separation"; in this work not only vapor–liquid equilibria, but also equilibria between any phases, including liquid, liquid crystals, etc., are considered.) At $x = x_b$ (Fig. 3(b)), the 1/2 transition occurs in a certain temperature range. In Fig. 3(c) ($x = x_c$), phases 1 and 2 are separated by a miscibility gap with strictly vertical phase boundaries.

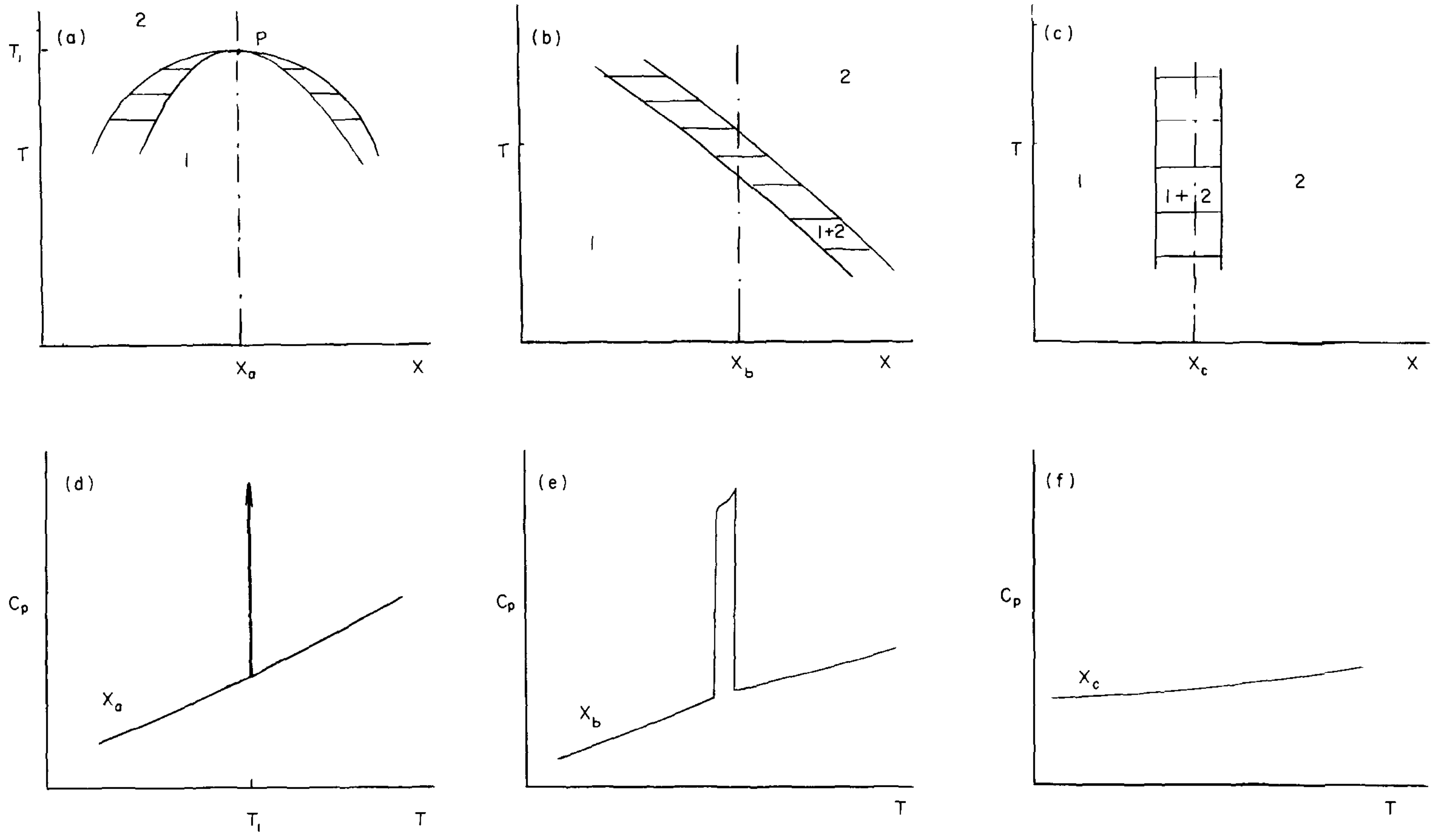

Fig. 3. Theoretical heat capacity behavior for isopleths x_a, x_b, x_c: (a), (b), (c), fragments of the phase diagram for x_a, x_b, x_c; and (d), (e), (f), the temperature dependence of the heat capacity of the system, respectively.

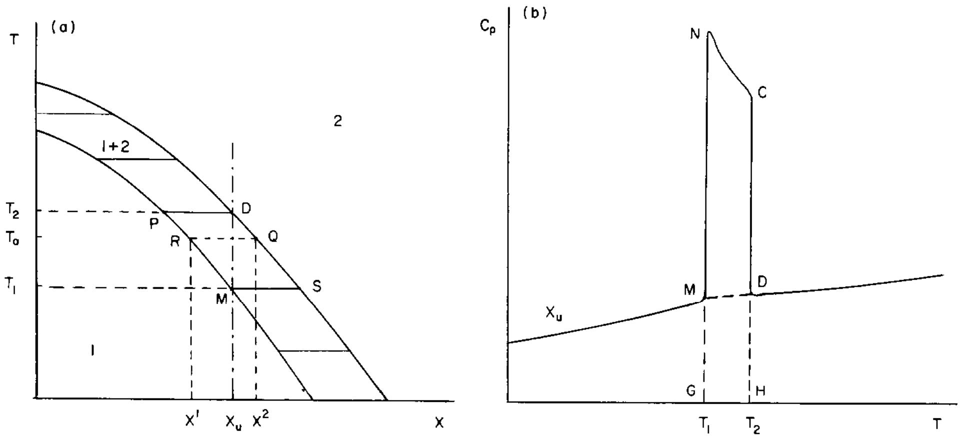

Fig. 4. (a) A fragment of a phase diagram and (b) the temperature dependence of a theoretical heat capacity for the composition $x = x_u$ for a binary system with a transition from phase 1 to phase 2 taking place in the T_1–T_2 interval. MD, a segment of a straight line. The area MNCD corresponds to ΔH_{trs}; area GMDH corresponds to $\Delta H'$.

A thermodynamic relation for the heat capacity of a biphasic two-component system is known [30]. For a system, Fig. 4(a), of gross molar composition x_u, containing at some temperature T_a, m^1 moles of phase 1 (molar composition x^1, molar specific heat C_p^1) and m^2 moles of phase 2 (molar composition x^2, molar specific heat C_p^2), $m^1 + m^2 = 1$, the molar heat capacity is given by

$$C_p(1+2) = \sum_{\alpha=1}^{2} m^\alpha C_p^\alpha + T \sum_{\alpha=1}^{2} m^\alpha g_{xx}^\alpha (\mathrm{d}x^\alpha/\mathrm{d}T)_p^2 \qquad (1)$$

where $(\mathrm{d}x^\alpha/\mathrm{d}T)_p$ is the shift of the α-phase composition with isobaric temperature variation, i.e. the slope of the α-phase boundary, and g_{xx}^α is the second derivative of the α-phase molar Gibbs free energy with respect to composition ($\alpha = 1, 2$) [30]. The values of g_{xx}^α are usually not known, but eqn. (1) allows us to predict qualitatively the heat capacity behavior if some information on the location of the phase boundaries is available [31,32].

Let us consider the enthalpy changes taking place in mixtures of compositions x_a, x_b and x_c, with temperature change for constant x.

At the invariant point (P in Fig. 3(a)), the two phases can coexist at only a single temperature T_i. The theoretical C_p value is infinite (Fig. 3(d)), and a sharp peak is observed in the DSC curves [18,32]. The 1/2-phase transition in a binary system occurs in the same way as an isothermal transition in a pure substance, and its transition enthalpy can be easily found by experiment.

If the boundaries of the biphasic region are strictly vertical (Fig. 3(c)), the derivatives $(\mathrm{d}x^1/\mathrm{d}T)_p$ and $(\mathrm{d}x^2/\mathrm{d}T)_p$ equal zero. For this specific case, the second term of eqn. (1) disappears, and the heat capacity of the heterogeneous system (Fig. 3(f)) is equal to the sum of the specific heats of the phases in equilibrium. As the temperature is raised for a biphasic mixture of composition x_c, the heat submitted to the system is spent only on heating the coexisting phases. The masses of the phases are the same, and no transformation of one phase into another takes place.

The case depicted in Fig. 3(b) can be considered to be intermediate between the two described above. Both the phase transition and the coexistence of the phases occur in the temperature interval T_1–T_2, and both effects make contributions to $C_p(1+2)$. The heat capacity of the heterogeneous system of composition x_b is given by eqn. (1), and both terms of the equation are non-zero and finite. Finite heat capacity jumps are observed at T_1 and T_2, when a homogeneous system becomes biphasic [18, 32].

Because the first term of eqn. (1) reflects the enthalpy spent on the heating of coexisting phases, it appears to be logical to suggest that the second term is responsible for the phase-transition heat effect. The enthalpy of a non-isothermal phase transition can then be defined as

$$\Delta H_{\mathrm{trs}}^{(\mathrm{u})} \overset{\mathrm{def}}{=} \int_{T_1}^{T_2} \left[C_p(1+2) - \sum_{\alpha=1}^{2} m^{\alpha} C_p^{\alpha} \right] \mathrm{d}T \qquad (2)$$

In order to find the transition enthalpy for the composition considered ($x = x_u$), it is necessary to know, in addition to $C_p(1+2)$, the specific heats of the phases coexisting at all the temperatures in the T_1–T_2 interval, i.e. the C_p values of the mixture at the curves MP and SD in Fig. 4(a).

The temperature dependence of the value $C_p'(T) = m^1C_p^1 + m^2C_p^2$ would serve here as a baseline. The equalities $C_p'(T_1) = C_p^1(T_1)$ and $C_p'(T_2) = C_p^2(T_2)$ are clear. For a great number of transitions, the temperature dependence of C_p' might be close to linear. The area delineated by the curve of the system's heat capacity and by a segment of a straight line drawn between the initial and final points of the transition (MNCD in Fig. 4(b)) can then be attributed to the enthalpy of a non-isothermal phase transition. The enthalpy spent on heating the phases in equilibrium, $\Delta H' = \int_{T_1}^{T_2} C_p'\,\mathrm{d}T$, corresponds to the area GMDH. Therefore, a generally accepted practice of drawing a baseline for peaks of this kind in calorimetric experiments could be justified. In the Results section below, the linearity of C_p' will be tested and ΔH_{trs} evaluated for a transformation of a liquid crystalline phase into an isotropic liquid.

Two-phases–one-phase transition following an invariant three-phase transformation

A binary system with a phase diagram presented in Fig. 5(a) undergoes a eutectic phase reaction $0 + 1 \rightleftharpoons 2$ at a temperature T_e. The heat capacity

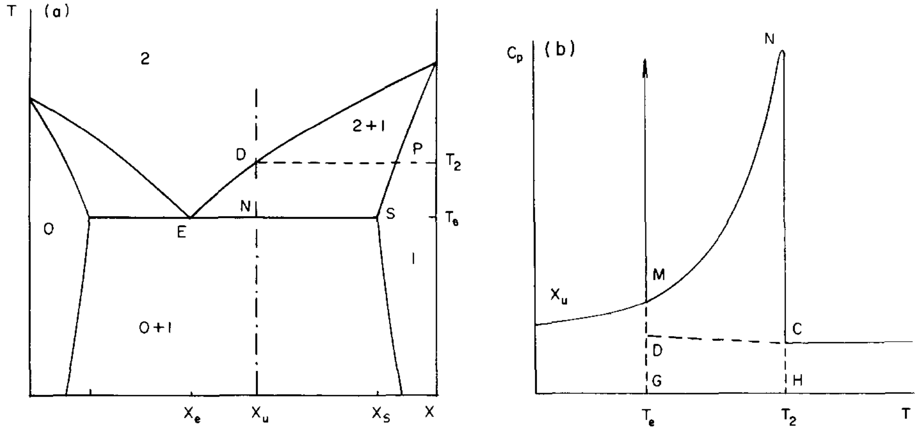

Fig. 5. A system with a eutectic phase reaction $0 + 1 \rightleftharpoons 2$ at a temperature T_e: (a) phase diagram; (b) theotetical heat capacity of the mixture with $x = x_u$. The arrow indicates $C_p = \infty$ at the eutectic temperature. MN represents the C_p of the biphasic $(1 + 2)$ system. DC is an example of C'_P, the sum of the specific heats of coexisting phases.

behavior of eutectic-type systems has been discussed earlier [18, 32]. For a mixture of gross molar composition x_u, the theoretical C_p value is infinite at T_e; when the biphasic system becomes homogeneous ($T = T_2$), a finite heat capacity jump occurs (Fig. 5(b)). The heat capacity of the system in the two-phase state in the T_e–T_2 interval is given by eqn. (1).

The transition observed at T_e is invariant; the composition dependence of its enthalpy yields the Tamman triangle [33].

The problem is to decide which thermodynamic quantities should be used to describe the phase transition taking place at temperatures above T_e. It is reasonable to apply the same definition as in the above case of a one-phase–one-phase transformation

$$\Delta H_{\mathrm{trs}}(\mathrm{u}) \overset{\mathrm{def}}{=} \int_{T_e}^{T_2} \left[C_p(1+2) - \sum_{\alpha=1}^{2} m^{\alpha} C_p^{\alpha} \right] \mathrm{d}T \qquad (3)$$

subtracting the contribution of the enthalpy spent on heating the coexisting phases from the total enthalpy change in the T_e–T_2 interval (the enthalpy of the eutectic reaction is not included). Then one must measure the specific heats of phases 1 and 2 at their boundaries SP and ED, and calculate their sum, $C'_p = m^1 C_p^1 + m^2 C_p^2$, in order to draw what would be a "baseline" for this mixture (Fig. 5(a)).

However, in the case considered in the previous section above, the transition started and finished with a system in a homogeneous state. Here the system is homogeneous only at the end of the transformation, at T_2. At this temperature, $m^1 \rightarrow 0$ and C'_p tends to $C_p^2 = C_p(T_2)$, i.e. to point C in Fig. 5(b).

At the beginning of the transition, at a temperature just above T_e (when the eutectic transition has already taken place and the heating of the system is continued), a biphasic state exists: the mixture of gross composition x_u consists of m^1 moles of phase 1 ($x = x_s$) and m^2 moles of phase 2 ($x = x_e$), $m^1 + m^2 = 1$. In ref. 31, it was shown that the heat capacity of the biphasic system in the general case exceeds the sum of the specific heats of the phases in equilibrium. This stems from the fact that the second term in eqn. (1) is non-negative

$$T \sum_{\alpha=1}^{2} m^\alpha g^\alpha_{xx} (\mathrm{d}x^\alpha / \mathrm{d}T)^2_p \geqslant 0 \qquad (4)$$

due to the quadratic dependence upon the derivative $(\mathrm{d}x^\alpha/\mathrm{d}T)_p$, and to g^α_{xx} being positive due to the phase stability requirement. This term could be zero at the beginning of the transition only if both derivatives, $(\mathrm{d}x^1/\mathrm{d}T)_p$ and $(\mathrm{d}x^2/\mathrm{d}T)_p$, are zero, i.e. if both phase boundaries, ED and SP in Fig. 5(a) are strictly vertical at points E and S. This is not the case for the system considered. Consequently, the value of $C_p(1+2)$ at a temperature just above T_e (corresponding to point M) exceeds the value of C'_p, the sum of the specific heats of coexisting phases; and the baseline at this temperature will be lower than point M, e.g. the C'_p value will correspond to some point D in Fig. 5(b). Therefore, the enthalpy of the univariant $(1+2)/2$ phase transition following a eutectic phase reaction is given by the area MNCD. Whether the temperature dependence of C'_p (line DC in Fig. 5(b)) is linear or not is determined by the phase diagram and by the heat capacity behavior at the phase boundaries. The area GDCH will then correspond to $\Delta H' = \int_{T_e}^{T_2} C'_p \, \mathrm{d}T$.

An example of the determination of C'_p and ΔH_{trs} by DSC for this kind of transition, according to definition (3), is given below.

Experimental

The non-ionic surfactants *n*-decyldimethylphosphine oxide and *n*-dodecyldimethylphosphine oxide ($C_nH_{2n+1}P(CH_3)_2O$, abbreviated to C_nPO, $n = 10, 12$) were purified by sublimation in a vacuum. The purity was better than 99.5 wt.% and 99 wt.% for $C_{10}PO$ and $C_{12}PO$ as given by a standard DSC purity determination. Twice-distilled water was used.

DSC traces were recorded using a Setaram DSC-111 instrument at heating rates $\phi = 2$, 1, 0.5, 0.25 and 0.1 K min^{-1}. Samples were prepared by weight and sealed in steel cells. Between 10 and 20 DSC runs were performed for each sample. To exclude the influence of the broadening of the DSC peak due to instrumental effects, the temperature intervals of the phase transitions were found for several scanning rates below 0.5 K min^{-1}, and then extrapolated to zero heating rate; correspondingly, the heat capacity values at the final transition temperatures were obtained by extrapolation of the experimental C_p values to $\phi = 0$. For the heat capacity measurements (at $\phi = 2$, 1 and 0.5 K min^{-1}), additional runs for two empty cells were performed prior to filling the sample cell. The heat capacity of twice-distilled water measured in the interval 295–360 K differed from the reference data [34] by less than 0.5% at $\phi = 2\,K\,\text{min}^{-1}$, 1% at $\phi =$ 1 K min^{-1}, and 2% at $\phi = 0.5$ K min^{-1}. The uncertainty of the C_p data for the surfactant–water mixtures was considered to be 3% for homogeneous states and 3–5% for heterogeneous states.

RESULTS

One-phase–one-phase transitions

A transition from a liquid crystalline lamellar (Lam) phase to an isotropic liquid (I) phase is observed in the $C_{12}PO–H_2O$ system (Fig. 6). The transition is invariant at $x_{\text{inv}} = 0.148$ (x is the molar fraction of surfactant) and $T_{\text{inv}} = 372.0$ K; for this mixture the peak of the Lam/I transition in the DSC curve is narrow and sharp, and the transition temperature is a maximum [20]. This isothermal transformation can be treated analogously to phase transitions in one-component systems, and its enthalpy can be precisely measured: $\Delta H_{\text{trs,inv}} = (0.148 \pm 0.002)$ kJ mol^{-1}. Enthalpies and heat capacities are expressed in units per mole of mixture.

The Lam/I transitions for other compositions take place in certain temperature intervals, $\Delta T = T_2–T_1$. The heat capacity of a mixture of

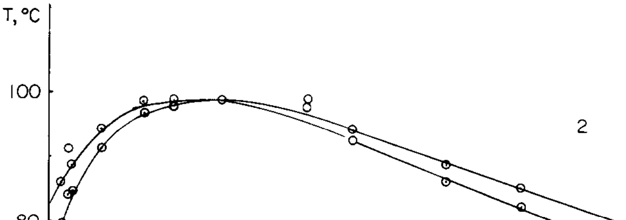

Fig. 6. A fragment of the phase diagram of the $C_{12}PO–H_2O$ system (x is the molar fraction of $C_{12}PO$). Phase 1 is the lamellar phase; phase 2 is isotropic liquid; 1 + 2 is the biphasic region. The lamellar/liquid transition is isothermal at $x_{\text{inv}} = 0.148$ and $T_{\text{inv}} = 372.0$ K. For $x_u = 0.301$, the transition takes place in the interval 343.6–348.2 K.

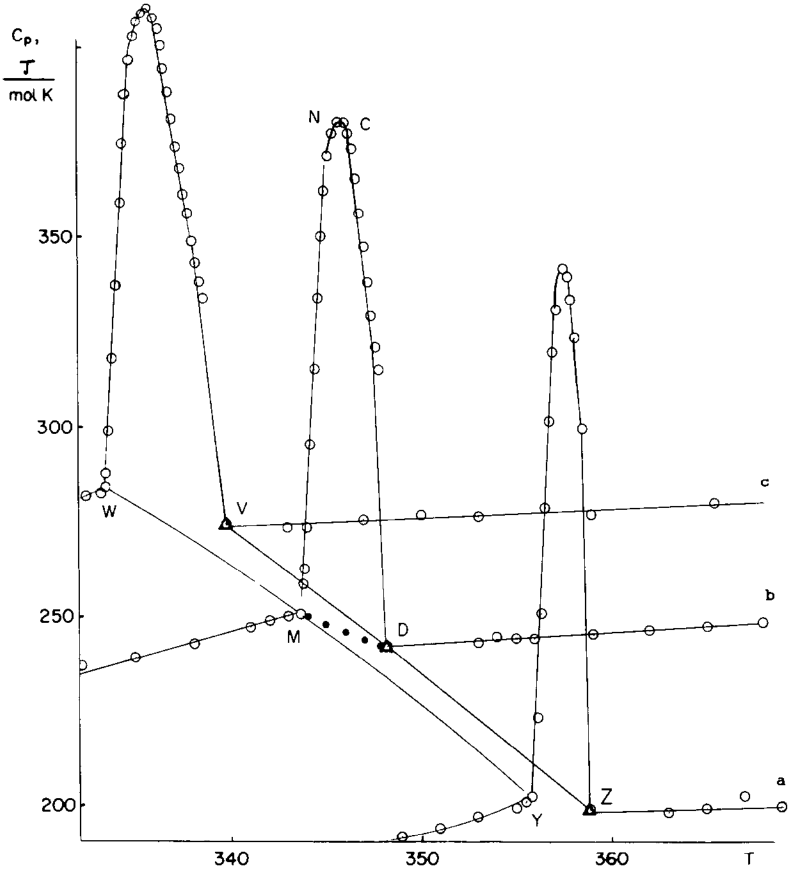

Fig. 7. Experimental molar heat capacities of the $C_{12}PO$–H_2O system plotted against temperature for compositions x, molar fraction of $C_{12}PO$: a, 0.240; b, 0.301; c, 0.352 (open circles). W, M, Y are the initial and V, D, Z the final points of the lamellar/liquid transition. The lines WMY and VDZ are the temperature dependences of C_p of the system at the boundaries of the lamellar and liquid phases, respectively. The triangles are the values found by extrapolation of experimental C_p values to zero heating rate. The solid circles are the values of C_p' (Table 2).

composition $x_u = 0.301$ and that of two mixtures of adjacent compositions were measured to determine the enthalpy of the univariant phase transition at x_u (Fig. 7). Table 1 gives the experimental specific heats of the mixtures at the initial and final transition temperatures. Curves WMY and VDZ are plotted through these points in Fig. 7, which gives the temperature dependences of C_p of the system at the boundaries of phases 1 and 2, $C_p^1(T)$ and $C_p^2(T)$ (1, Lam; 2, I).

For the sample considered ($x = x_u$), the phase process takes place in the temperature interval 343.6–348.2 K. At any temperature in this interval, one can find the specific heats of the coexisting phases from the curves WMY and VDZ in Fig. 7 and the masses of the phases from the phase

TABLE 1

Molar heat capacities C_p of the dodecyl-dimethylphosphine oxide ($C_{12}PO$)–H_2O system of composition x (molar fraction of $C_{12}PO$) at the initial T_1 and final T_2 temperatures of the Lam/I transition

x	T_1 (K)	$C_p(T_1)$ (J mol^{-1} K^{-1})	T_2 (K)	$C_p(T_2)$ (J mol^{-1} K^{-1})
0.240	355.8	202	358.9	199[a]
0.301	343.6	251	348.2	242[a]
0.352	333.3	284	339.8	274[a]

[a] Extrapolated to $\phi = 0$.

diagram (Fig. 6). This allows us to calculate C_p', the sum of the specific heats of the coexisting phases (Table 2). For the transition considered, the temperature dependence of C_p' is practically linear (MD in Fig. 7).

The enthalpy of the non-isothermal phase transition can then be determined according to definition (2), as the area limited by the curve of the heat capacity of the system and by the segment of a straight line drawn between the initial and final points of the transition (MNCD in Fig. 7); the total enthalpy change in the transition interval is the integral of the heat capacity of the system. For $x = x_u$, the following values are obtained (kJ mol^{-1}): $\Delta H_{trs} = 0.50 \pm 0.02$; $\Delta H' = 1.13 \pm 0.05$; and $H(348.2) - H(343.6) = 1.6 \pm 0.1$.

For the given mixture, the temperature interval of the Lam/I transition ΔT is 4.6 K, which exceeds ΔT for the majority of univariant transitions from one phase to another observed in the system. One can expect a linear temperature dependence of C_p' for smaller values of ΔT. In subsequent measurements, the enthalpies of the non-isothermal phase transitions in the system were obtained by integration of the peaks in the DSC curves, and

TABLE 2

Masses (m^1, m^2) and molar heat capacities (C_p^1, C_p^2) of phases coexisting at temperature T in the $C_{12}PO$–H_2O system of gross composition $x_u = 0.301$: 1, Lam; 2, I phase; m^1 and m^2 are obtained from the phase diagram (Fig. 6) and C_p^1 and C_p^2 are obtained from the curves WMY and VDZ in Fig. 7; C_p' ($=m^1C_p^1 + m^2C_p^2$) is the sum of the specific heats of phases coexisting at temperature T

T(K)	m^1	C_p^1 (J mol^{-1} K^{-1})	m^2	C_p^2 (J mol^{-1} K^{-1})	C_p' (J mol^{-1} K^{-1})
344.0	0.91	249.5	0.09	258	250
345.0	0.73	246	0.27	254.5	248
346.0	0.54	242	0.46	251	246
347.0	0.32	238	0.68	247	244
348.0	0.08	234	0.92	243	242

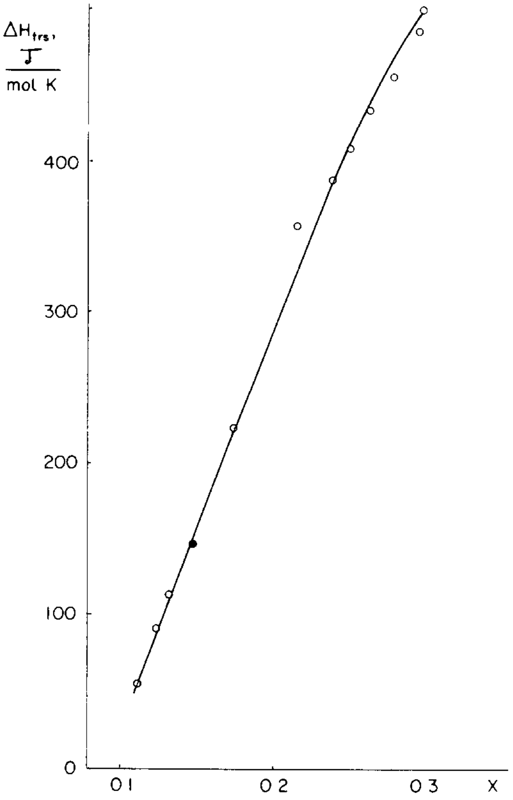

Fig. 8. Enthalpies of isothermal (●) $\Delta H_{trs,inv}$ and non-isothermal (○) phase transitions from lamellar phase to isotropic liquid in the $C_{12}PO$–H_2O system plotted against concentration.

the baseline was taken as a straight line between the initial and final points of the peak.

The enthalpies of the Lam/I transition thus obtained are plotted against concentration in Fig. 8. One can see that ΔH_{trs} is a continuous function of concentration and the value of the enthalpy of the isothermal Lam/I phase transformation $\Delta H_{trs,inv}$ (indicated by a solid circle) is consistent with the values of ΔH_{trs} for univariant Lam/I transitions.

Two-phase–one-phase transition following a eutectic phase reaction

A eutectic phase reaction, crystals (C) + Lam $\rightleftharpoons$ I, takes place in the $C_{10}PO$–H_2O system at $T_e = 308.7$ K. The compositions of the phases involved in the phase reaction are $x(\text{Lam}) = 0.317 \pm 0.003$, $x_e = 0.338 \pm 0.003$ and $x(C) = 1.0$. (In this work pure $C_{10}PO$ is considered to be involved in the phase reaction; however, the uncertainty of the $x(C)$ determination is 0.06 [19].) A fragment of the phase diagram of the system is shown in Fig. 9.

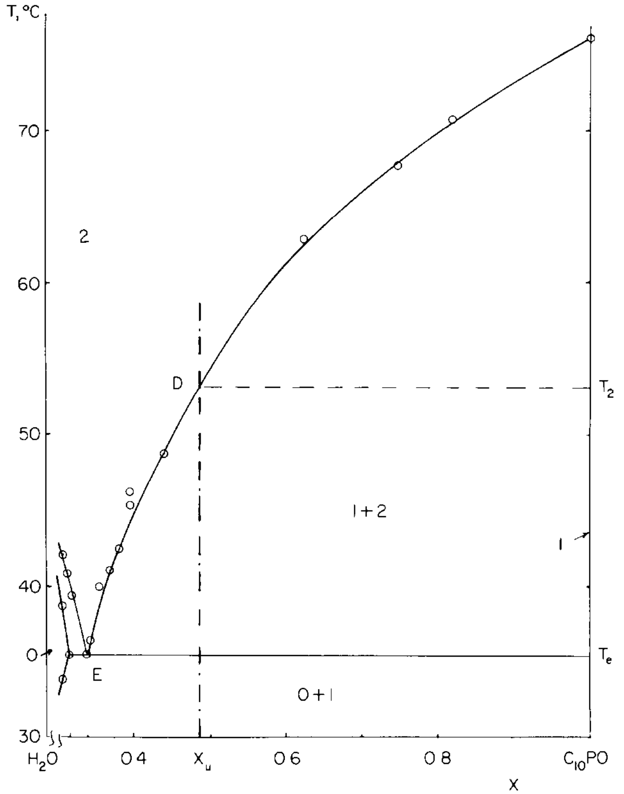

Fig. 9. A fragment of the phase diagram of the $C_{10}PO$–H_2O system: 0, lamellar phase; 1, crystals; 2, isotropic liquid. Points are transition temperatures obtained by DSC. T_e (=308.7 K) is the temperature of the eutectic phase reaction $0 + 1 \rightleftharpoons 2$. T_2 (=327.6 K) is the final temperature of the transition (1 + 2)/2 for $x_u = 0.487$.

The enthalpy of the eutectic phase transition ($x = x_e$) is $\Delta H_{trs}(e) = 1.3 \pm 0.1$ kJ mol^{-1}. The enthalpy of melting (at $T = 349\,K$) of pure crystalline $C_{10}PO$ is $\Delta H_{trs} = 28 \pm 1$ kJ mol^{-1}.

The composition under consideration is $x_u = 0.487$. Experimental values of the heat capacity of this mixture are reproduced in Fig. 10 (open circles). At $T < T_e$, the Lam and C phases coexist; at $T > T_e$, crystalline and liquid phases are in equilibrium, and the system becomes homogeneous at $T_2 = 327.6$ K. To find the enthalpy of the (C + I)/I transition according to definition (3), the heat capacity of the liquid phase at the ED boundary (Fig. 9) and the heat capacity of the crystalline $C_{10}PO$ in the T_e–T_2 interval must be known. Experimental results for C_p values of the system at the liquidus curve and for C_p values of the pure surfactant are presented in Fig. 10. The sum of the specific heats of coexisting phases C_p' is calculated for several temperatures (Table 3) and presented in Fig. 10 (solid circles). The line connecting these points MD would be a baseline for this heat effect.

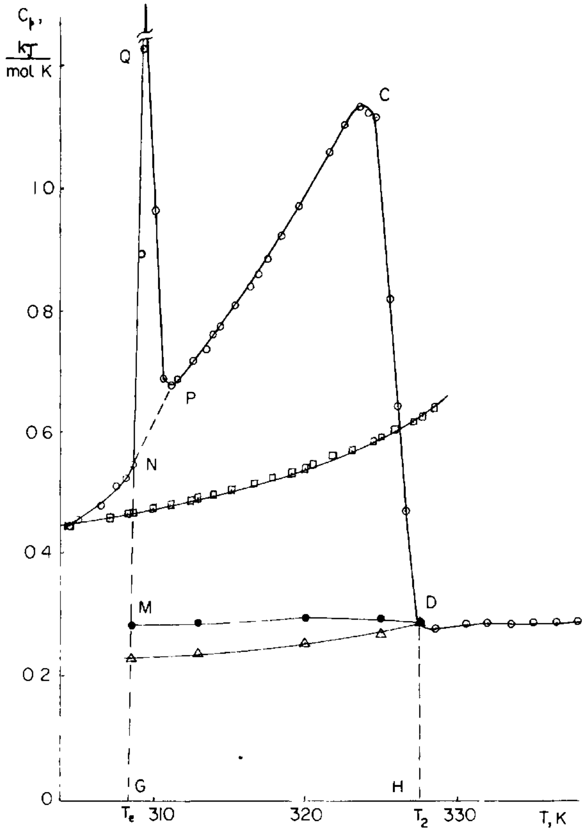

Fig. 10. The temperature dependence of the heat capacities in the $C_{10}PO–H_2O$ system: ○, C_p for the mixture with $x_u = 0.487$; NQP, peak of the eutectic phase transition; PC, C_p of the system in the biphasic (crystals + liquid) state; △, C_p^2, heat capacity of the system at the boundary (ED in Fig. 9) of the liquid phase; □, C_p^1, the heat capacity of pure crystalline $C_{10}PO$; ●, C_p', the sum of the heat capacities of the coexisting liquid and crystalline phases. The area MNPCD corresponds to the enthalpy of the non-isothermal (1 + 2)/2 phase transition; MDHG gives the enthalpy spent on the heating of the coexisting phases.

TABLE 3

Compositions (x^1, x^2), masses $(m^1, m^2;\ m^1 + m^2 = 1)$ and molar heat capacities $(C_p^1,\ C_p^2)$ of phases coexisting at a temperature T in the $C_{10}PO–H_2O$ system of gross composition $x_u = 0.487$; C_p^2 values are extrapolations to $\phi = 0$. C_p' $(=m^1C_p^1 + m^2C_p^2)$ is the sum of the specific heats of the phases coexisting at temperature T; phase 1, crystals; phase 2, liquid

T(K)	x^1	m^1	C_p^1 (J mol^{-1} K^{-1})	x^2	m^2	C_p^2 (J mol^{-1} K^{-1})	C_p' (J mol^{-1} K^{-1})
308.7	1.0	0.23	468	0.338	0.77	231	284
313.0	1.0	0.20	492	0.356	0.80	238	290
320.0	1.0	0.14	543	0.406	0.86	256	295
325.0	1.0	0.06	595	0.452	0.94	276	296
327.6	1.0	0.0	627	0.487	1.0	290	290

One can clearly see that the baseline does not start at point P (the end of the eutectic transition), being located instead at much lower C_p values, because the heat capacity of the biphasic (liquid + crystals) system exceeds the sum of the specific heats of liquid and crystalline phases.

The area of the sharp peak at T_e, NQP, corresponds to the enthalpy of the eutectic transition at x_u, $\Delta H_{trs}(e, x_u)$; the Tamman triangle for this phase reaction has been reported earlier [18]. The enthalpy of the univariant phase transition (C + I)/I for the system of composition x_u, $\Delta H_{trs}(u)$, is given by the area NMPCD. The enthalpy spent on heating the coexisting phases corresponds to the area GMDH. Thus, the total enthalpy change for this system in the T_e–T_2 interval (including the enthalpy of the eutectic reaction), $H(T_2) - H(T_e) = (22 \pm 1)$ kJ mol^{-1}, contains the following contributions (kJ mol^{-1}): $\Delta H_{trs}(e, x_u) = 1.00 \pm 0.03$; $\Delta H_{trs}(u) = 15.5 \pm 0.6$; and $\Delta H' = 5.5 \pm 0.2$.

One can see that the $\Delta H'$ and $\Delta H_{trs}(u)$ values are of the same order of magnitude, and it is the non-isothermal transition enthalpy that makes the greatest contribution to the total enthalpy change. The value of $\Delta H_{trs}(u)$ lies between the values of the enthalpy of melting of the pure surfactant and of the eutectic reaction.

DISCUSSION

There is no doubt that quantitative enthalpy characteristics of non-isothermal phase transitions are needed. In ref. 15, for instance, ΔH_{trs} values for transitions of this kind were used to determine the practical applicability of mixtures of thermotropic liquid crystals in optical devices. As shown above, literature references describe different ways of drawing baselines for non-isothermal heat effects. It is important to understand which thermodynamic quantity is being measured before we try to consider the influence of various factors of instrumental origin (those related to the device, to the heating rate, to the thermal conductivity of the sample, etc. [35]) on the shape of the DSC curves and on the baseline.

The definition of ΔH_{trs} considered here is based on a rigorous relation for the heat capacity of heterogeneous systems [30], and all the quantities used in it are measurable by experiment.

For the Lam/I transformation in the $C_{12}PO$–H_2O system that occurs over a 4.6 K interval, the baseline turned out to be linear; the values of ΔH_{trs} for non-isothermal phase processes obtained using such a baseline were a continuous function of concentration and were consistent with the value of ΔH_{trs} at the invariant point. One can suggest that the sum of the specific heats of coexisting phases would be a linear function of temperature for many non-isothermal one-phase–one-phase transitions encountered in binary systems, especially if they occur in a relatively narrow temperature interval (less than 10 K). These are some reasons for the justification of the common practice of taking a segment of a straight line between the initial and final points of a peak as a baseline, and determining the transition enthalpy as the area limited by the DSC curve and this baseline.

However, we cannot apply the same procedure for a non-isothermal two-phase–one-phase transition preceding or following an invariant phase reaction. It has been demonstrated here both theoretically and using an experimental example, that when applying definition (3), the initial point of the baseline lies lower than the initial point of the peak observed after the eutectic melting (if the phase boundaries are not strictly vertical). As a result, the area corresponding to ΔH_{trs} has a shape that is rather different from that obtained using previous methods of determining this transition enthalpy.

For an evaluation of ΔH_{trs}, the definition (3) requires information on the phase diagram and additional C_p measurements. It may be found in practice that it is not convenient to determine this transition enthalpy, and the phase process will be characterized by the temperatures T_e and T_2 and by the heat capacity jump occurring when the biphasic system becomes homogeneous.

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