THEORETICAL AND EXPERIMENTAL INTERPRETATION OF THE SIGNALS FROM ΔITA

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Abstract

Discontinuous isoperibolic thermal analysis (ΔITA) is a phase diagram investigation technique applicable to organic components systems (with at least one liquid phase). The elementary signal is composed by the evolution of the temperature of the system *vs.* time after a composition shift. A theoretical analysis and a mathematical modeling of this signal show that the overall enthalpy exchanged multiplied by a proportional factor can be obtained. From different experiments, evidence is given that this semi-quantitative calorimetric measurement is reliable. Thus, ΔITA allows consistent and accurate descriptions of phase diagrams and is a real relative calorimetric measurement technique.

Introduction

Discontinuous isoperibolic thermal analysis (ΔITA) is a phase diagram investigation technique applicable to organic component systems (with at least one liquid phase). The technique is already available, nevertheless an improved understanding of the phenomena will result in a larger quantity of consistent information retrieved from the experimental data.

Principles of the technique

A heterogeneous system (kept in isoperibolic conditions) is shifted out of equilibrium state by discontinuous additions of a homogeneous thermostated liquid (pure solvent, mixture of miscible solvents, solution). After each injection the system returns spontaneously to an equilibrium state via physical phenomena such as dilution, dissolu-

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tion, crystallization, demixion, etc… These phenomena imply enthalpy changes which lead to temperature variations of the system. A high sensitive thermometer (resolution 10^{-3} K) linked to a computer gathers the temperature data (ΔT) *vs.* time (t). One addition of liquid implies one elementary signal. A sudden temperature variation is followed by a slow and spontaneous relaxation towards the initial temperature (Fig. 1).
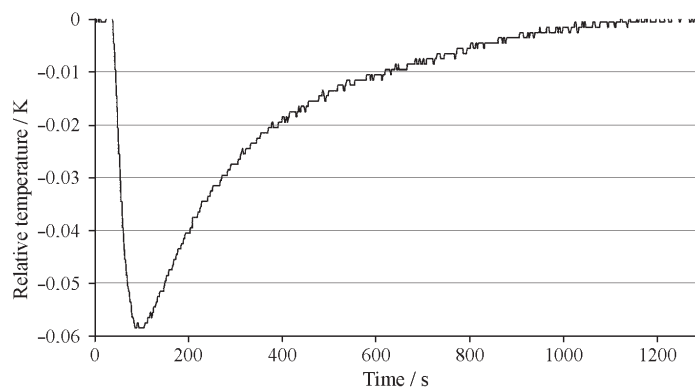

Fig. 1 Typical elementary signal

The aim of this paper is to give an interpretation and a modeling of the experimental signal from ΔITA.

Interpretation

Two energy changes can be contemplated during an elementary signal:
- the overall enthalpy variation of the system due to reaction(s): ΔH
- the heat exchanged between the system and its direct isothermal environment: Q

During the interval between the liquid addition and the end of the relaxation, the evolution of these two energies is time dependent: $\Delta H(t)$ and $Q(t)$.

General interpretation

No assumptions are made about the number, the nature and the kinetics of the physical phenomena that occur, nevertheless the following hypotheses are assumed:

$Q(t)$ is controlled by the Newton's law:

$$\partial Q(t)/\partial t = -k\Delta T(t)$$

This statement has been experimentally checked (see 'The Newton's law').

$\Delta H(0)=0$ and $\Delta H(+\infty)$ is the total energy exchanged during the phenomena $\quad$ (1)

$$Q(0)=0 \text{ and } Q(+\infty)= -\Delta H(+\infty) \tag{2}$$

According to Newton's law:

$$\Delta T(t)\partial t = -\partial Q(t)/k \tag{3}$$

The total surface of an elementary signal is assimilated to the integration of $\Delta T(t)$ *vs.* time (from $t=0$ to $t=+\infty$): $I = \int_0^{+\infty} \Delta T(t)\partial t$

According to Eq. (3): $I = \int_0^{+\infty} -\frac{1}{k}\partial Q(t) \rightarrow I = -\frac{1}{k}\int_0^{+\infty}\partial Q(t) \rightarrow I = -\frac{1}{k}(Q(+\infty)-Q(0))$

According to Eqs (1) and (2):

$$I = -\frac{Q(+\infty)}{k} = \frac{\Delta H(+\infty)}{k} \tag{4}$$

This result allows the interpretation of the signals. Indeed the cumulated integration values (ΣI) plotted *vs.* the cumulated quantities of liquid added lead to the determination of discontinuities in the evolution of ΔH *vs.* composition. It can be related to the topology of the phase diagram. An example is given below with a ternary system (+)/(−) solute and solvent (Figs 2 and 3).
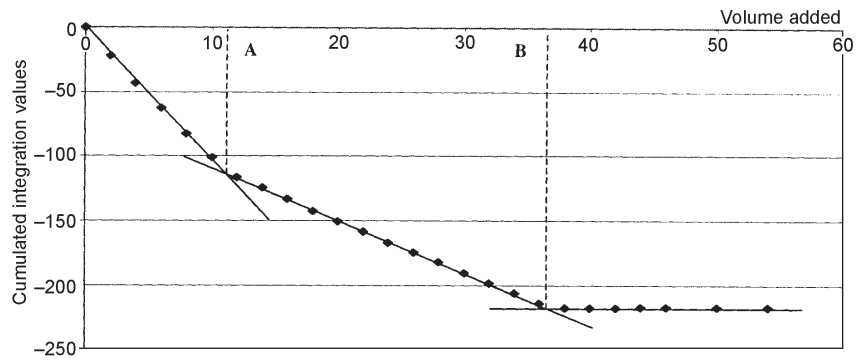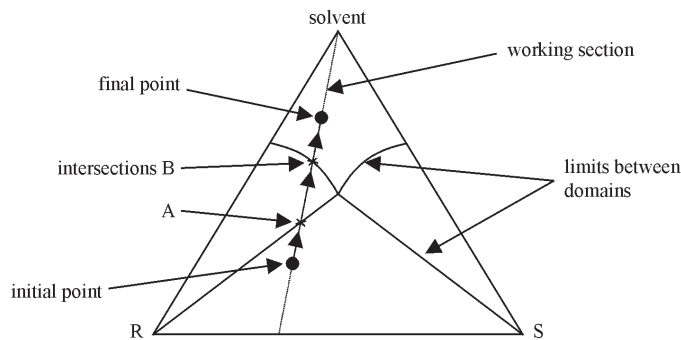

Fig. 2 Exploitation plot

Fig. 3 Corresponding phase diagram (example of a conglomerate)

Mathematical modeling for a simple case

By considering a two phase binary system (component X and solvent S; X(solid) in equilibrium with its saturated solution) with addition of pure solvent, it is possible to build a model of an elementary signal from simple assumptions.

At the equilibrium state there are neither visible dissolution nor crystallization, but they really occur with the same opposite kinetics.

Assumptions

The dissolution has a first order kinetic depending on the solvent concentration. The crystallization has a first order kinetic depending on the solute concentration.

$$rd=kd[S] \tag{5}$$

(rd – dissolution rate, kd – dissolution kinetic constant, $[S]$ – solvent concentration).

$$rc=kc[X] \tag{6}$$

(rc – crystallization rate, kc – crystallization kinetic constant, $[X]$ – solute concentration).

At the equilibrium state:

$$[X]=Csat \tag{7}$$

($Csat$ – solute concentration at the saturation).

$$rd=rc \tag{8}$$

(no visible dissolution nor crystallization)

At the equilibtium state and according to Eqs (5)–(8):

$$Csat=[S]kd/kc \tag{9}$$

By adding a volume v of solvent to the system containing a liquid phase with a volume V, the system is shifted out of equilibrium.

Assumptions

The addition of liquid is instantaneous and it first dilutes instantaneously the liquid phase.
$[S]$ remains roughly constant.

The dissolution becomes visible:

$$R=\partial[X]/\partial t=rd-rc \tag{10}$$

(R – visible dissolution rate)

According to Eqs (5), (6) and (9):

$$R=kc(Csat-[X]) \tag{11}$$

According to (10) and (11):

$$\partial[X]/\partial t + kc[X] = kcCsat \tag{12}$$

The resolution of the differential Eq. (12) leads to $[X]$ as a function of time:

$$[X](t) = Csat(1 - v/(V+v)\,\exp(-kct)) \tag{13}$$

and then to the appearing quantity of X in solution as a function of time $(n(X)(t))$:

$$n(X)(t) = Csatv(1 - \exp(-kct)) \tag{14}$$

Assumptions

There are two energy changes:

- the enthalpy exchanged because of the dissolution $\Delta H(t)$
- the heat exchanged between the system and its direct environment because of the temperature variation: $Q(t)$

The enthalpy change depends on the dissolution enthalpy for one mole of X and on the appearing quantity of X in solution.

The heat exchanged is controlled by the Newton's law.

The system is in perfect isoperibolic conditions: its direct environment is perfectly isothermal.

For the calculations, the sign of $\Delta H(t)$ for the reaction medium is taken against the convention, indeed an endothermic dissolution implies a decreasing of the temperature of the reaction medium. So for an endothermic process, the enthalpy change is considered as positive for the reaction itself and negative for the reaction medium.

$$\Delta H(t) = \Delta Hmn(X)(t) \tag{15}$$

ΔHm – dissolution enthalpy for one mole of X

According to (14) and (15):

$$\Delta H(t) = \Delta HmCsatv(1 - \exp(-kct)) \tag{16}$$

The Newton's law describes the heat flow *vs.* time:

$$\partial Q(t)/\partial t = -k\Delta T(t) \tag{17}$$

$\Delta T(t)$ – relative temperature of the system or temperature difference between the system and its direct environment; k: constant >0.

The relative temperature is given by the total energy exchanged by the system and by its heat capacity:

$$\Delta T(t) = (Q(t) + \Delta H(t))/C_p \tag{18}$$

C_p – heat capacity of the system at constant pressure.

According to (17) (Newton's law) and to (18):

$$\partial Q(t)/\partial t = -k(Q(t) + \Delta H(t))/C_p \tag{19}$$

$$\partial Q(t)/\partial t + kQ(t)/C_p = -k\Delta H(t)/C_p \tag{19'}$$

The resolution of the differential equation (19') thanks to (16) leads to the expression of $Q(t)$:

$$Q(t)=\Delta H(+\infty) \ (k/(kcC_p-k)(\exp(-k/C_p t)-\exp(-kct))+\exp(-kt/C_p)-1) \qquad (20)$$

Checking the limit conditions: $Q(0)=0$ and $Q(+\infty)=-\Delta H(+\infty)$
The total enegy exchanged can be now expressed according to (18) and (20):

$$Q(t)+\Delta H(t)=\Delta H(+\infty)kcC_p/(kcC_p-k)(\exp(-kt/C_p)-\exp(-kct)) \qquad (21)$$

And finally the expression of the relative temperature *vs.* time according to (18) and (21):

$$\Delta T(t)=\Delta H(+\infty)kc/(kcC_p-k)(\exp(-kt/C_p)-\exp(-kct)) \qquad (22)$$

The exploitation of the theoretical elementary signal (total integration of $\Delta T(t)$ *vs.* time) can be expressed according to (22):
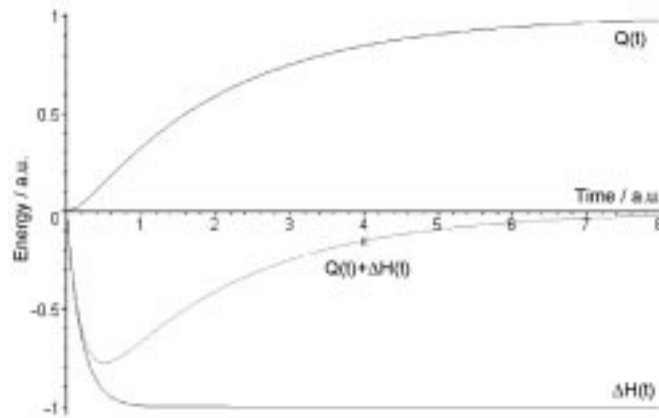

Fig. 4 Decomposition of the total energy exchanged

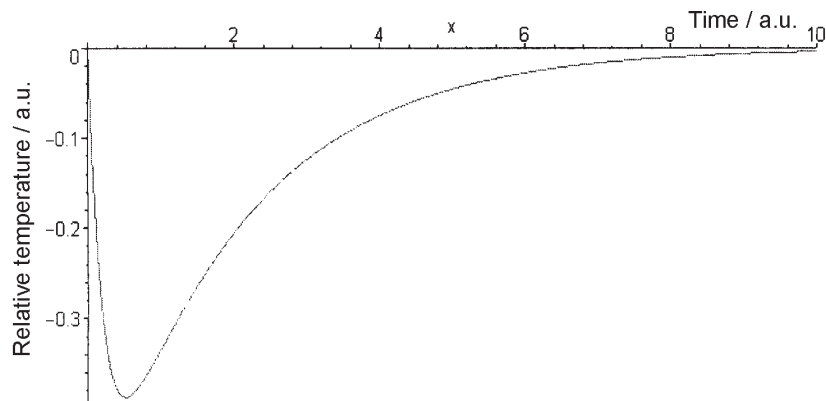**Fig. 5** Theoretical elementary signal of a simple dissolution

$$\int_0^{+\infty}\Delta T(t)\partial t=\int_0^{+\infty}\Delta H(+\infty)kc(kcC_{\mathrm{p}}-k)(\exp(-kt/C_{\mathrm{p}})-\exp(-kct)))\partial t \qquad (23)$$

$$\int_0^{+\infty}\Delta T(t)\partial t=\Delta H(+\infty)/k \qquad (23')$$

The expression (23') is the interpretation of the integration of an elementary signal in a special case. It fits with the general interpretation.
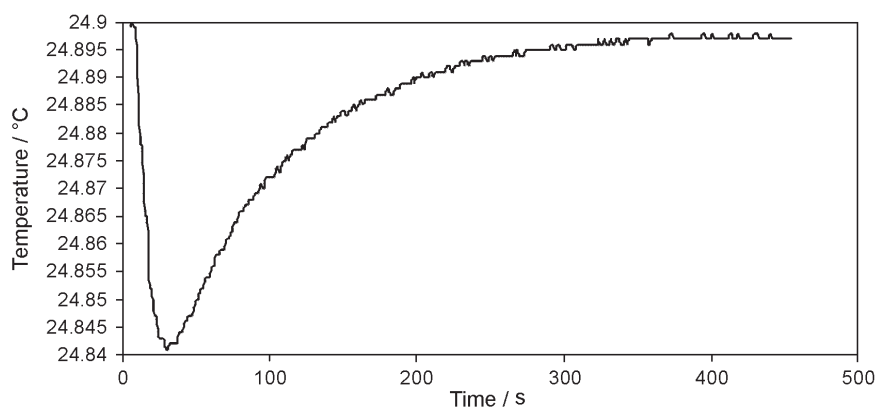

Fig. 6 Experimental elementary signal of a simple dissolution in a binary system

As a comparison an experimental elementary signal of a simple dissolution in a binary system is shown (Fig. 6).

The Newton's law

This law is the fundamental statement of all the theoretical interpretations of ΔITA signals.

Brief recall of the theory

There always exists a spontaneous heat exchange between two non-isolated systems (with different temperatures) in contact. This exchange, according to the second law of thermodynamics, occurs always from the 'hot' system to the 'cold' system.

The Newton's law describes the heat flow:

$$\frac{\partial Q(t)}{\partial t}=-k\Delta T(t)$$

where $Q(t)$ is the total amount of heat exchanged (J), t is the time (s), $\Delta T(t)$ is the temperature difference between the two systems (K) and k is a positive constant related to the wall between the two systems (J K^{-1} s^{-1}).

If the studied system is the 'hot' one, $\Delta T(t)$ is positive and $\partial Q(t)/\partial t$ is negative (the system loses energy). If the studied system is the 'cold' one, $\Delta T(t)$ is negative and $\partial Q(t)/\partial t$ is positive (the system receives energy). In both cases the law is applicable.

The relative temperature $\Delta T(t)$ can directly be related to the heat exchanged $Q(t)$:

$$\Delta T(t) = \frac{1}{C_p} Q(t) + \Delta T(0)$$

where C_p is heat capacity of the studied system, and so: $Q(t)=C_p\Delta T(t)-C_p\Delta T(0)$

The derivative expression $vs.$ time is

$$\frac{\partial Q(t)}{\partial t} = C_p \frac{\partial \Delta T(t)}{\partial t}$$

and according to the Newton's law:

$$C_p \frac{\partial \Delta T(t)}{\partial t} = -k\Delta T(t)$$

The integration of this differential equation leads to:

$$\ln \Delta T(t) = -k/C_p t + \ln \Delta T(0)$$

So if the plotting of $\ln\Delta T(t)=f(t)$ values draws a straight line (slope: $-k/C_p$), the Newton's law is applicable.

A simple experiment has been run.

30 mL of 'hot' water are placed in isoperibolic conditions in the ΔITA apparatus linked to a 'cold' thermostatic system. The evolution of the temperature of the water is recorded $vs.$ time (Fig. 7).

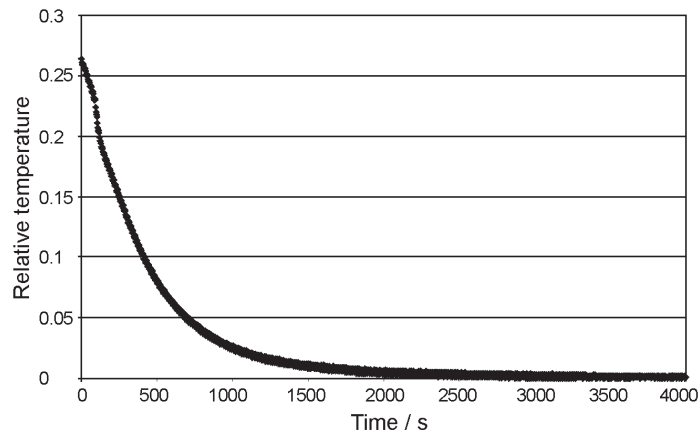Then the values $\ln\Delta T(t)=f(t)$ are plotted (Fig. 8):

Fig. 7 Relative temperature $vs.$ time during a relaxation process
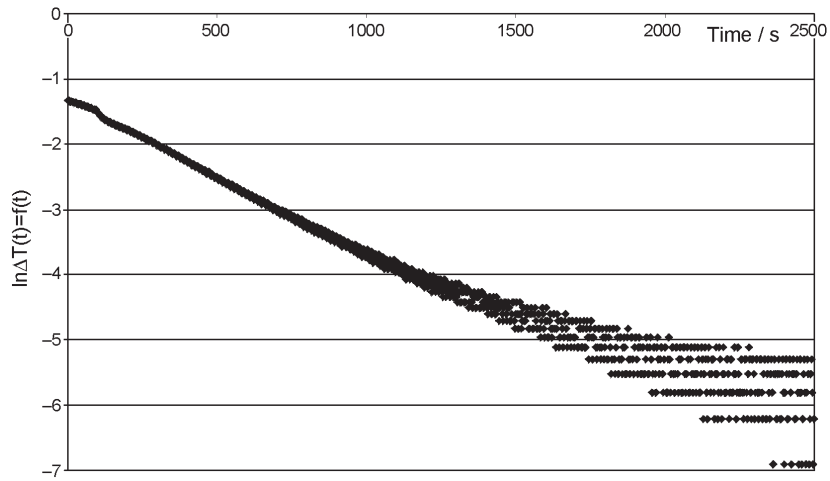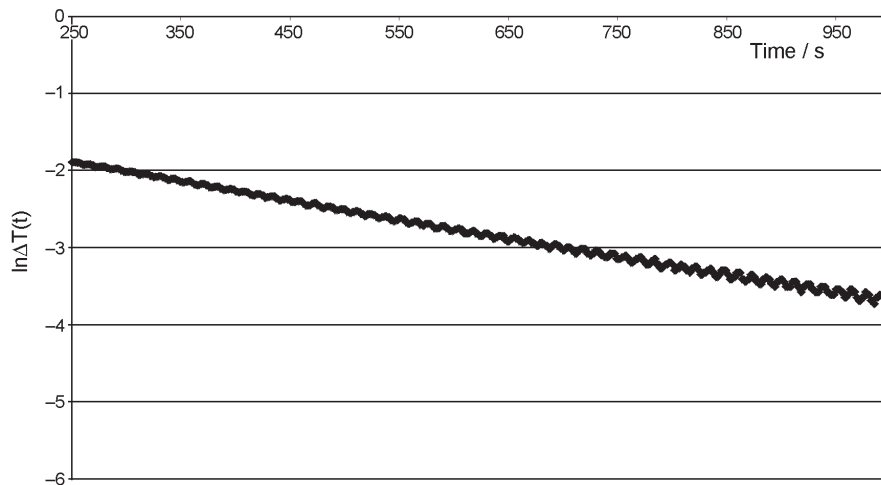
Fig. 8 $\ln\Delta T(t) = f(t)$

Fig. 9 Consistent part of the plot

The first part of this curve (from t=0 to 250 s) is not straight. It is due to the perturbation of the sample installation, the thermostatic system has not reached a stable activity yet.

The last part of the curve (from t=1000 s to the end) has a special aspect. The dispersion of the dots corresponds to the limit detection of the thermometer (10^{-3} K). Indeed the numerical analysis of experimental data loses consistency as the relative error taken into account increases. After a while the thermometer is measuring T=0 K which leads to indefinite value (ln(0)…). The consistent part of the plot ($250 < t < 1000$) is represented (Fig. 9) and a linear regression is calculate on this interval.

The regression on the consistent part ($250 < t < 1000$):

$$k/C_p = 4.89 \cdot 10^{-6} \text{ s}^{-1} \text{ (slope)}$$

$$r = 0.9969$$

The dots draw a consistent straight line, so the Newton's law seems to be applicable with ΔITA experiments.

Relative calorimetry

The result implies that ΔITA is a relative calorimetric technique. Indeed the proportional factor $1/k$ is supposed to be constant during the whole experiment (around 20 elementary signals) and from an experiment to another. Such assumptions have been experimentally checked as detailed below.
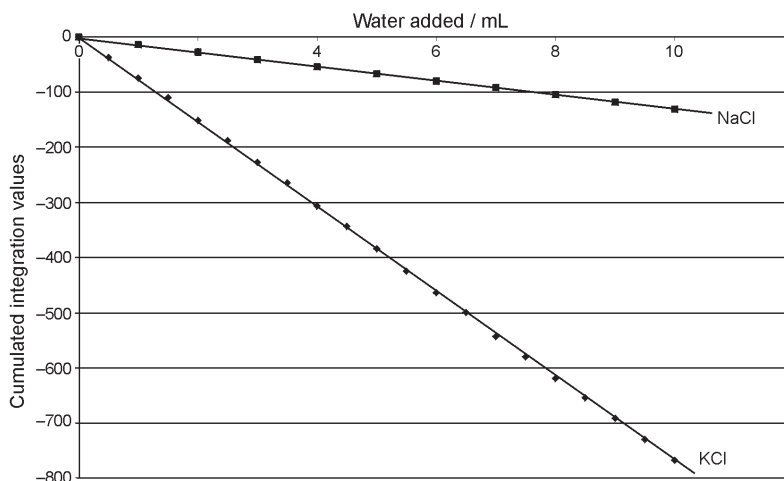

Fig. 10 Exploitation plots for NaCl/H$_2$O and KCl/H$_2$O, dissolution in the biphasic domain (saturated solution+crystals; 298.15 K)

Two experiments were run on reference systems (NaCl/H$_2$O and KCl/H$_2$O): additions of pure solvent (H$_2$O) in the suspensions at 298.15 K. As they are isobaric, isothermal binary systems with two phases, they have no degree of freedom: the dissolution enthalpy is directly proportional to the amount of solvent added. So the cumulated integration values *vs.* the total amount of solvent added must describe a straight line (Fig. 10).

The correlation values show that the curves are straight lines:

- NaCl: $r = 0.999739$
- KCl: $r = 0.999928$

so k remains constant during an experiment.

The values of the enthalpies of dissolution at saturation per mL of water for NaCl and KCl are given in literature [1, 2]:

- $\Delta H\mathrm{d}(\mathrm{NaCl}) = 12$ J mL^{-1} and $\Delta H\mathrm{d}(\mathrm{KCl}) = 69$ J mL^{-1}
- Their ratio is $\Delta H\mathrm{d}(\mathrm{KCl})/\Delta H\mathrm{d}(\mathrm{NaCl}) = 5.7_5$

The experimental slopes are:

- Slope (NaCl) $= -13.2$ K s mL^{-1} and slope (KCl) $= -77.0$ K s mL^{-1}
- Their ratio is slope (KCl)/slope (NaCl)$=5.8_3$

The similar values of the two ratios mean that the value of k is the same in these two experiments:

- NaCl: $k = 0.91$ J K^{-1} s^{-1}
- KCl: $k = 0.90$ J K^{-1} s^{-1}

These results show the consistency of the relative calorimetry by ΔITA.

Conclusions

ΔITA has especially been designed to build phase diagrams in the case of organic components systems. ΔITA is now an operative technique, the phase diagram topologies are obtained just from a qualitative exploitation of the experimental data.

The enhanced interpretation of the physical phenomena that occur during an experiment leads to more information from the experimental data. ΔITA has proved to be able to perform semi-quantitative calorimetric measurements. Such information may help in understanding the heterogeneous equilibria that control the phase diagram topology.

References

1 N. Hubert, R. Solimando, A. Pere and L. Schuffenecker, Thermochim. Acta, 294 (1997) 157.
2 G. Castronuovo, V. Elia, M. Niccoli and F. Velleca, Thermochim. Acta, 320 (1998) 13.