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*Calorimetry*

# SOME CONSIDERATIONS OF COHERENCY IN TOPOENERGETIC TERMS

## I. High-resolution mixing calorimetry (HRMC) experiments on aqueous solutions

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The spatial coherency of composite structures is discussed in topoenergetic terms by considering mixing experiments on water and aqueous solutions with HRMC. Two series of experiments are presented: on normal and shaken successively diluted aqueous solutions of $Na_3PO_4 \cdot 12H_2O$ with methanol as structure developer, and on the solubility behaviour in water of a narrow size fraction of KCl crystals irradiated at 546 nm for different time multiples of 5 seconds. The amplitude of relative standard deviation of the integral mixing energy as a function of mixing time shows the contribution of different elementary processes by revealing the specific spectrum of the composite structure in water and aqueous solutions.

**Keywords**: high-resolution mixing calorimetry (HRMC), topoenergetic terms

## Introduction

The composite structure of systems undergoing transformation was the starting point of topoenergetic principles [1]. This means that a spatially modulated

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coherency exists in any system, even at equilibrium, but specifically developed by a process of transformation. The inert and transforming components are the two main phases defining both the nature and the amplitude of the process [2, 3]. Calorimetry was the first measuring system for which topoenergetic principles were applied and progressively developed, and this was not accidental, because of at least the following reasons:

(i) calorimetry allows the easy demonstration of an energy circuit in a bond diagram representation [1, 2, 4];

(ii) it also reveals basically temperature-driven processes which can be comparatively represented in Arrhenius and topoenergetic universal terms;

(iii) the process polarity, as an important new notion, is directly associated with the polarity of the heat flow of the two components [5], and (iv) calorimetry represents a universal measuring system because any transformation process is accompanied by a heat flow.

However, there are some cases for which the transformation processes give no heat flow effect in the external measuring system, and these correspond to the existence of an inductive element in the coupling impedance between the two components [6].

Structural and energy aspects of coherency arise in topoenergetic terms as a coupling between the inert and transforming elements [7]. The amorphous-crystalline coupling has been thoroughly studied for polyethylenes [5–7], and extended to a large variety of materials, even aqueous solutions and chemically pure water [8, 9]. Coherency has been revealed as a basic aspect of material behaviour in different measuring systems. This coupling appears to govern the cold fusion phenomena and involves the overall inner circuit of the sample [10].

The composite structure of liquids, especially water an aqueous solutions, occupies a special place in our recent series of intensive studies, and we start the series on coherency by considering their behaviour in HRMC experiments, because these are very simple, suggestive and rapid.

Classical principles on calorimetric measurements of mixing under rigorous adiabatic conditions [11] are now removed in the HRMC technique [8], to reveal the nonreproducibility of the results by high resolution (as a different notion in respect of high sensitivity) and reproducible standard conditions imposed by topoenergetic principles [12]. The dispersion of the results is a reverse measure of the inner coherency of the two mixing substances. Thus, we can reveal under the best conditions the specific or nonspecific potentials governing the inner coherency of tested samples.

Two suggestive cases of HRMC experiments on water and aqueous solutions are considered in this work, which actually correspond to the domain of 'pathological science', as Douglas Morrison called the nonreproducible and unstable results of cold fusion experiments [13]. These are the solubility behaviour in standard water of KCl crystals irradiated according to Comorosan's technique, and the mixing behaviour of successively diluted aqueous solutions of $Na_3PO_4 \cdot 12H_2O$ obtained in the normal way and according to the homeopathic technique with standard methanol. In these cases, water and aqueous solutions represent the developer (with standard composite structure) and the tested sample, respectively.

## Theoretical background

The conversion of a single (unimodal) transformation process can be revealed in the HRMC measuring system by the differential heat flow, $w(t)$, or by the integral energy, $E(t)$. If we neglect the induction period associated with the attainment of the heat flow maxima, the integral energy can be described by the equation

$$E(t) = E_o(1 - \exp(-t/t_o)) \qquad (1)$$

and this corresponds to the majority of practical cases. However, for almost all these cases, the apparatus resolution reveals the induction time, $t_i$, for which $E(t)$ becomes

$$E(t) = E_o(1 - \exp(-(t+t_i)/t_o)) \qquad (2)$$

For $t_i << t_o$, Eq. (1) remains valid.

The significance of the kinetic parameters ($E_o$, $t_o$, $t_i$) determining the solubility behaviour of the two tested samples as unitary system under the chosen standard experimental conditions (or the ontogeny) can be established by taking into account that $E_o$ represents the process amplitude. For different experimental conditions in which the same nature of the behaviour is preserved, but with different amplitudes, affine relationships of the type

$$E_o = a(t_o \text{ or } t_i) + b \qquad (3)$$

can be established, defining the phylogenic parameters ($a$, $b$) [12].

These change in time of solubility behaviour is revealed by the HRMC technique through measurement of the integral energy at suitably chosen moments with respect to the starting instant of breaking the glass bubble [8]. On repetition of the experiment for identical specimens, each $E(t)$ value is accompanied by a relative standard deviation. $\sigma(t)$, which theoretically results from Eq. (1) as

$$\sigma(t) = 100\,(1/E)(\mathrm{d}E/\mathrm{d}t) = 100\,(\exp(-t/t_o))/(t_o(1 - \exp(t/t_o))) \qquad (4)$$

expressed in percentages.

Typical fits of $E(t)$ and $\sigma(t)$ for the unimodal case are represented in Fig. 1. It is important to point out that both functions have a strictly monotonous time de-

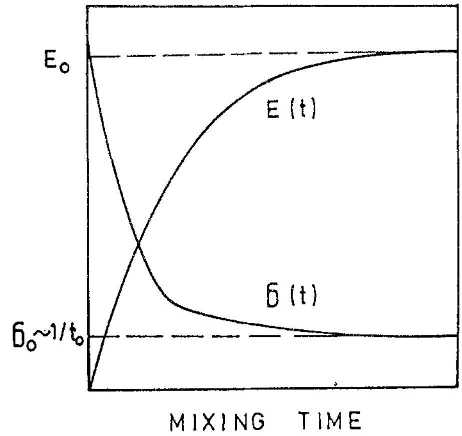

**Fig. 1** Typical fits for the integral energy of mixing $E(t)$ and the relative standard deviation $\sigma(t)$ associated to a unimodal mixing process

pendence. The practical importance of $\sigma(t)$ consists in the fact that, by comparing different samples with disperse individual values of $E(t)$, it is possible to make differences only for $\sigma(t)$, through both its values and the shape of the time dependence, which often deviates from the above theoretical prediction.

## Experimental details

The HRMC apparatus and the working procedure for study of the solubility behaviour were recently described in detail [8]. In the meanwhile a highly accurate integrator for $E(t)$ values was adapted to the $w$(t) signal by a dc voltage-to-frequency converter(0–±10 V to 0–10 kHz) and a universal counter with 7 digits. The $E(t)$ measurements were accurate up to $2\times10^{-5}$ J, but we usually neglected the last two digits due by their high rate of variation during the mixing process, but with correct stability at the beginning of the experiments. The HRMC analyses were carried out at 30.0°C, and Fig. 2 schematically represents the typical specimens used in the two series of experiments, denoted as A and B.

A. Two series of 8 aqueous solutions, each of $Na_3PO_4 \cdot 12H_2O$, were prepared by successive dilution of a 1 *M* stock solution with a dilution ratio of 1/2 and 1/100, respectively. The first series was obtained by simple addition of solvent without any agitation. The second was subjected to vigorous shaking according to a homeopathic technique, by using an aluminium block 250 mm in diameter and 200 mm in height, with a cotton tissue on its top. Each solution of the two series was prepared and preserved at the same volume and in the same type (in size and shape) of glass. All solutions and MeOH as developer were kept at

30°C for 48 hours before HRMC analyses. Freshly distilled water was used for normal diluted series, and distilled water annealed at room temperature (not shaken) for approximately 3 months was used for shaken solutions. Five identical HRMC experiments for each solution were performed in order to determine $E(t)$ and $\sigma(t)$ values.

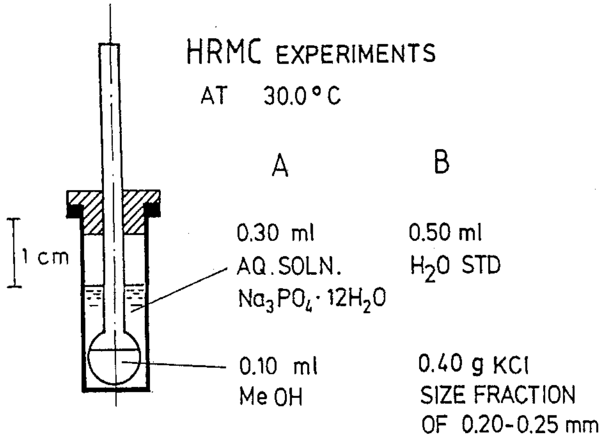

**Fig. 2** Schematical representation of the two series of mixing experiments called as A and B

B. The narrow size fraction of KCl crystals (analytical grade) of 0.20–0.25 mm was used. Amounts of 100 mg of such crystals were placed in a uniform single layer in identical cylindrical glass containers 50 mm in diameter and preserved in a desiccator over anhydrous $CaCl_2$. Each glass container was subjected to irradiation for a time multiple of 5 seconds with an accuracy of 0.1 s. The irradiation was performed at a wavelength of 546 nm by using a special device previously described in detail [14]. The samples of 40±0.1 mg were weighed in glass bubbles in natural light after their irradiation, but all samples were irradiated, weighed and HRMC analyzed in the same, rhythm, i.e. one irradiated sample a day. A reference sample of nonirradiated sample was analyzed before the irradiated sample on the same day. Freshly bidistilled water obtained during the first day of work was isolated in a special 300 ml glass jar for the total period of the experiments (10 days).

## Results and discussion

A. The mixing of EtOH and of MeOH with water are known to be very disperse processes. When alcohol is added to an open glass of water, agitation on the liquid surface is readily observable. The proportions of the two liquids chosen for the present experiments proved optimum in reducing such disperions of the results. The $E(t)$ values for the exothermal process of mixing are not so important for our discussion, and they are not taken into account. The values of $\sigma$ are represented in Fig. 3 for the two series of solutions as their change in time and as a function of dilution order at four conversion times.

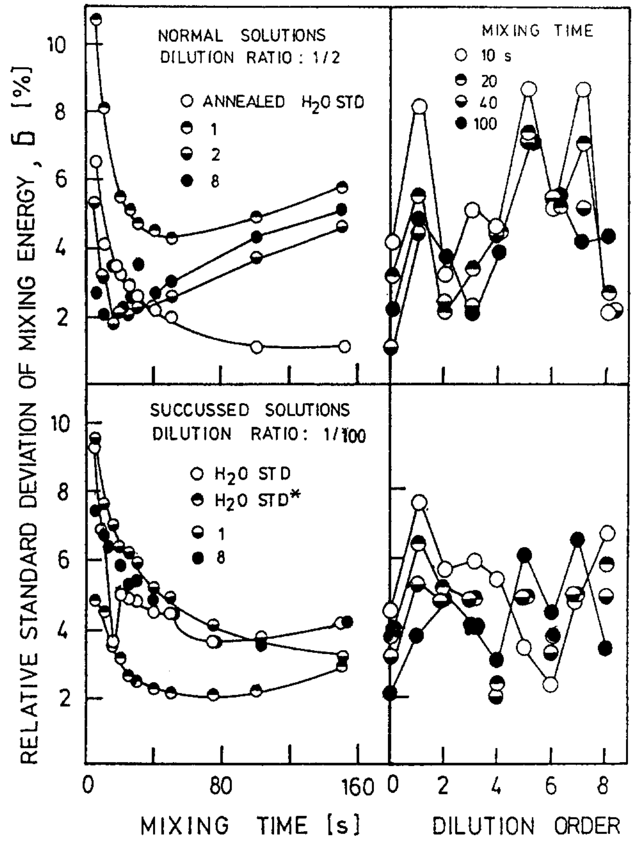

Fig. 3 Representation for the relative standard deviation values of the integral mixing energy as a function of mixing time and dilution order for the two series of successively diluted solutions of $Na_3PO_4 \cdot 12H_2O$ (series A of experiments)

We may notice first some basic differences for the $\sigma(t)$ dependences for the three types of water: freshly distiled ($H_2O$ STD), shaken ($H_2O$ STD$^*$) and annealed (ANN $H_2O$ STD). The annealing and shaking have the effect of equilibrating the composite structure of water by decreasing the $\sigma$ values in the following sequence:

$$H_2O\ STD > H_2O\ STD^* > ANN\ H_2O\ STD \qquad (5)$$

In addition, $H_2O$ STD shows an important deviation from the theoretical prediction of $\sigma(t)$. The high values and the appearance of parasite maximum can be assigned to a spectrum of the coupling of the transforming ($C_{tr}$) and the inert ($C_{in}$) components. The applied treatments specifically narrow this spectrum. A similar process was established in essentially crystalline and amorphous materials [6, 7, 15], even in the frozen state of water and electrolyte solutions.

Normal solutions show increasing $\sigma$ values after a prominent minimum relating to 10–50 seconds of conversion. If we consider that in the first stage of mixing the weakest coupling states are developed by the chemical etching effect of the developer, this minimum marks the beginning of development of stronger and stronger states. $H_2O$ STD clearly shows this separation, and on $Na_3PO_4 \cdot 12H_2O$ addition the separation increases, i.e. the first stage of weak coupling species is narrowed and the second stage increases. This increase represents the contribution of strongly coupled water molecules from the electrolyte solute.

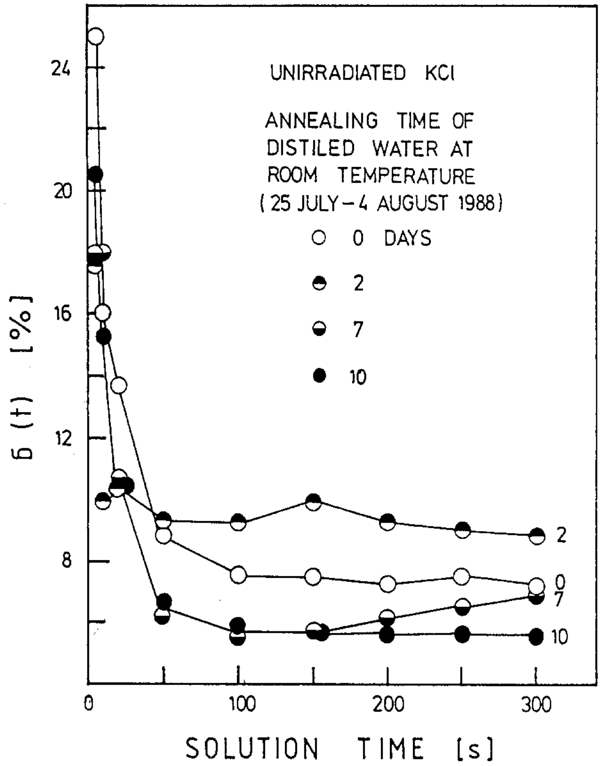

**Fig. 4** Relative standard deviation of integral mixing energy for $H_2O$ STD with unirradiated KCl as a function of mixing time at different moments of experiments in series B by annealing at room temperature

Shaken solutions show a broadening of the first stage due to the hardening process of the initial species.

Another important aspect corresponds to the oscillatory behaviour of the σ values as a function of dilution order for both series of solutions (see the left side of Fig. 3). The amplitude of these oscillations is smaller for shaken solutions, but the maxima are for the same orders: 1, 3, 5, 7.

B. The absolute values of *E*(*t*) (endothermal process) are also neglected for such mixing experiments. However, we may mention that the mean values at 300 seconds of mixing were 3.1 J or 77.5 J/g (KCl) = 5.78 kJ/mol (KCl) for the chosen molality of 80 g (KCl)/l = 1.073 mol/kg. The results reported under highly accurate adiabatic conditions show a value of 16.426 kJ/mol (KCl) for the molality up to 0.06 mol/kg at 30.0°C [16]. This comparison once again reveals the working principle of HRMC experiments in developing the solubility be-

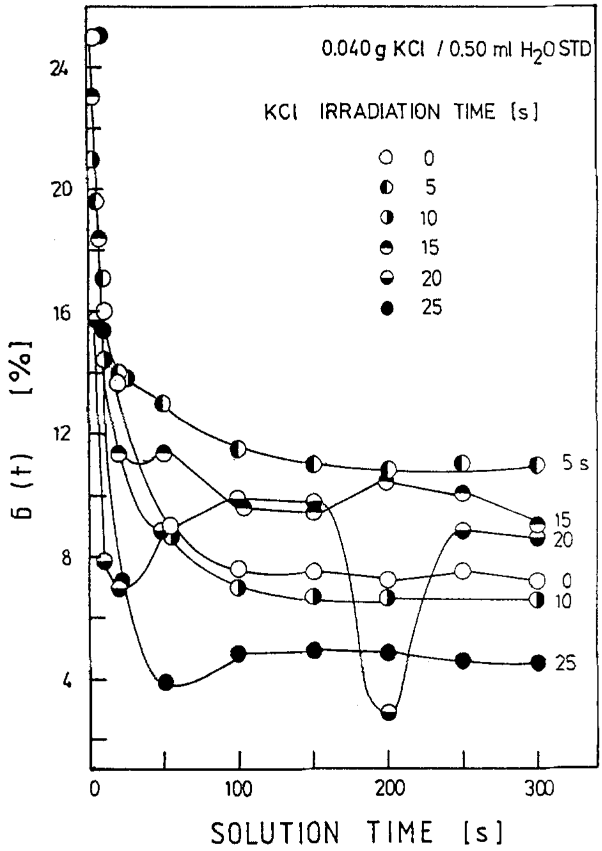

**Fig. 5** Relative standard deviation of integral mixing energy as a function of mixing time for $H_2O$ STD with KCl crystals irradiated for different times

haviour by its partial kinetics under very reproducible conditions (including the specific surface of the solute) and the high resolution of heat flow.

The solutbility behaviour of $H_2O$ STD as a function of annealing time at room temperature is represented in Fig. 4, considering nonirradiated KCl crystals as standard developer. We observe the narrowing of the first stage, but the appearance of parasite maxima on the second day of annealing and decreasing $\sigma$ values for the second stage on the subsequent days of annealing. These phenomena represent the contribution of a separation process of coupling species and the removal of unstable ones.

The changes in $\sigma(t)$ values obtained for all tested samples are compared in Fig. 5. Freshly bidistilled water and KCl at $t_{irr} = 0$ are taken as the reference system. The spectra of coupling species in water are specifically revealed by irradiated KCl samples. In order to demonstrate correct modifications induced by

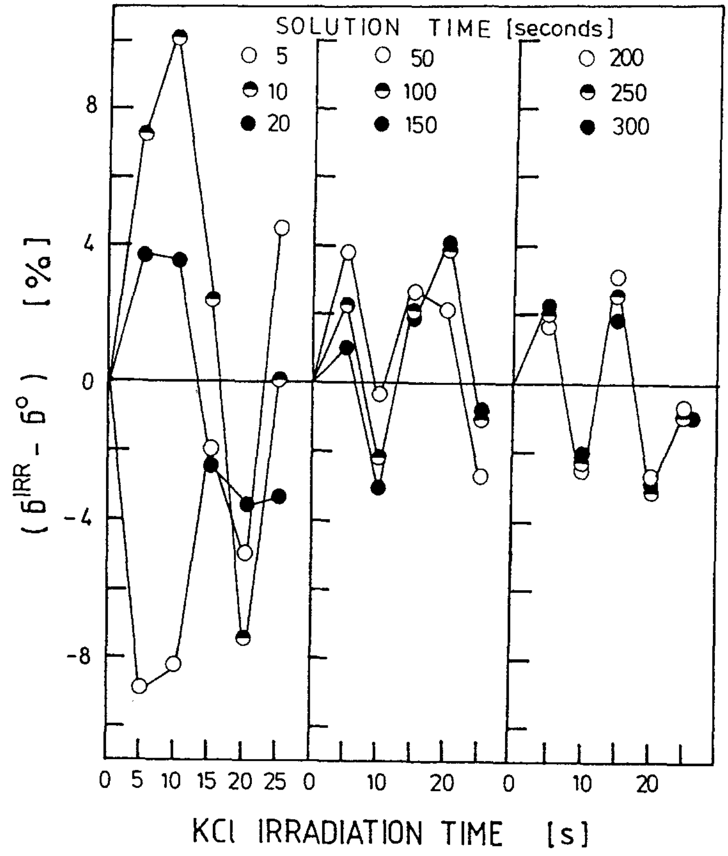

Fig. 6 Variation of ($\sigma^{irr}$–$\sigma^{0}$) as a function of irradiation time of KCl crystals for different moments of mixing

KCl irradiation, we must compare pairs of $\sigma(t)$ changes for irradiated ($\sigma_{irr}$) and nonirradiated ($\sigma_o$) crystals analyzed on the same day. These differences are represented in Fig. 6 as a function of irradiation time by comparatively grouping three conversion times on each section of the Figure. We may at once observe large oscillating variations in the first stage of mixing (0–20 seconds), which become stabilized and clearly show positive and negative maxima at subsequent times.

## Concluding remarks

The following conclusions may be drawn from the above results.

1. The solubility behaviour of an aqueous solution with a standard developer in a single (unimodal) exo or endothermal process reveals the spectrum of the coupling species between the transforming ($C_{tr}$) and inert ($C_{in}$) components in this system.

The structural model of an overall standard specimen given by topoenergetic working principles is represented in Fig. 7a. The kinetic entity ($C_{tr}$) is represented here as being of unique size, but in fact a polydispersion of it exists.

2. The transforming component of the sample involves the chemically reactive part of the aqueous solution etched by the developer. The inert component is rep-

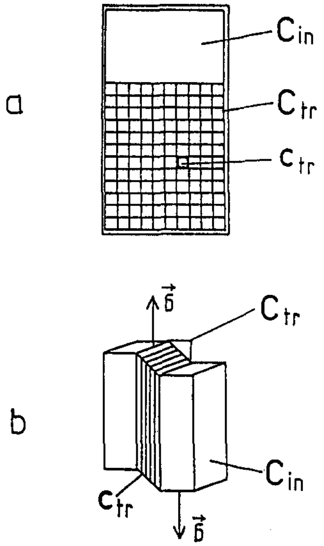

**Fig. 7** *a* Schematical representation of composite structure of the standard sample during a unimodal process of transformation. The kinetic entity ($C_{tr}$) is represented for simplicity as being of unique size.
*b* Structural model of the repeating unit in the paracrystalline composite structure of the sample under transformation

resented by highly ordered molecular clusters of water. Figure 7b schematically presents a structural model of the repeating unit of the paracrystalline order in the specimen of aqueous solution. "Crystalline" domains of $C_{in}$ are coupled with 'intercrystalline' domains by a disclinative state which accumulates specific shear stresses ($\vec{\delta}$). Direct evidence of this model was obtained for solid materials [2, 5, 6, 15], and even for frozen water [9], and it is also valid for liquids [3, 9]. This structural model could better explain the azeotropic mixture as a separation of pure liquid in $C_{in}$ domains and a stable mixture in $C_{tr}$. This phenomenon can be thoroughly studied by HRMC by considering the interaction of mixtures at different concentrations and specific developers.

3. Annealing and mechanical shaking represent treatments which govern the separation process between $C_{in}$ and $C_{tr}$ by narrowing the spectrum of the coupling species ($C_{tr}$).

4. Oscillatory behaviour as a result of such treatments is another important and general feature of solubility behaviour. This aspect mainly arises as in other measuring systems (see, for instance, capillary flow [17]) by a resonance phenomenon, because the sudden mixing process appears as a perturbation in the resonant cavity of the measuring cell. In the above-presented series A and B of experiments, the resonant effects of treatments applied to aqueous solutions and the developer result. This reveals that both mixing components have a composite structure.

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**Zusammenfassung** — Mittels HRMC von Wasser und wäßrigen Lösungen wurde durch Mischversuche die Raumkohärenz von Verbundstrukturen in topoenergetischen Termen diskutiert. Es werden zwei Reihen von Experimenten dargestellt. Die Amplitude der relativen Standarddeviation der vollen Mischenergie als eine Funktion der Mischzeit zeigt den Beitrag verschiedener Elementarprozesse durch aufschlußreiche Spektren der Verbundstruktur in Wasser und wäßrigen Lösungen.