

## **Solubility behaviour introducing Topoenergetic working principles**

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### ABSTRACT

The solubility behaviour of composite systems as starting point of topoenergetic principles is reviewed in general terms by considering the already existing databank mainly based on the 1-octanol/water partition coefficients and IUPAC series of Solubility Data. The new physical assignments of the basic notions (solute, solvent, composite system, kinetic entity, stability-compatibility, etc.) are defined again by considering kinetic aspects important for standardization of experimental conditions. New notions, quantities and quantitative relationships are presented for creation of databanks on new and more efficient working principles, including so-called "good metrology", allowing to obtain more reliable results and to detect more structural assignments.

### 1. INTRODUCTION

The main goal of this paper is to introduce and to point out important aspects of experimental conditions in which the basic experimental data (BED) are obtained in general and in particular for solubility behaviour of test-substances in 1-octanol/water mixtures. The first and for the moment the only aspect of measurements is represented by metrology, but although most of these mentioned aspects are generally known and accepted, they were not considered up to now for reliable results. The efforts should be made in view to improve at least the following aspects:

- The experimental conditions,
- The retrieval of obtained BED,
- The assignments of databanks.

We avoid deliberately to mention literature citations. It looks like a general lecture on a well-known topic, so specialists would not need definition on solvent or solute. Because this presentation is substantiated on a long and intensive experience, the specific examples considered in the next regular papers will be supported by previous results.

### 2.SOLUBILITY KINETICS AND SOLUTION MORPHOLOGY

1-octanol is representative for the amphiphilic behaviour, having the strong hydrophile -OH end group and the n-alkane chain as hydrophobe and lipophile. The molecular morphology of its aqueous solutions, strongly depends on temperature, mechanical history (mixing technique), concentration, pH, pX, etc. We are expecting to find in an equimolar solution, clusters of octanol with molecular distribution depending on these mainly mentioned parameters. It is important to remind that even pure water has a composite morphology dependent on its own history, so this adds to the above mentioned parameters.

What happens by addition in a such mixture (water/1-octanol = WOS) of a test substance with heteromolecular structure and having also an amphiphile behaviour.? The solubility kinetics univocally defines the final morphology of the final solution depending also on the mentioned parameters. These parameters governing this kinetics and the structure and properties of the final product, are called in classical non-equilibrium thermodynamics as **driving potentials**.

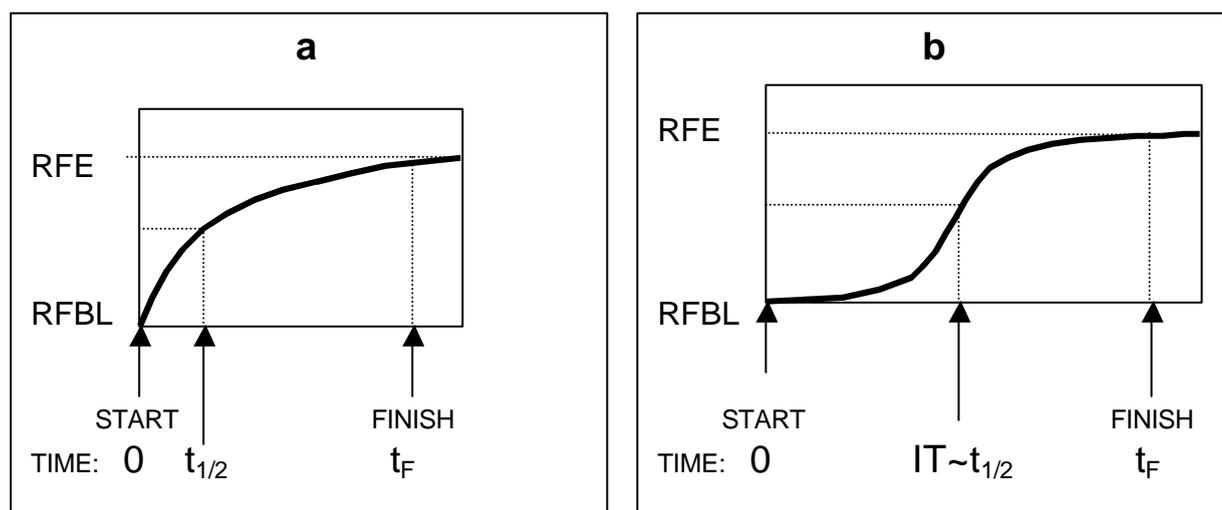
### 3.MEASURING SYSTEM AND STANDARD EXPERIMENTAL CONDITIONS (SOP)

We may conclude that there are two main ways for defining the solubility process: to measure its kinetic or to make direct structural analysis on the final morphology. One problem could arises: what is more important for practical purposes? It follows probably to see the answer in the future debates. For the moment, we must observe that the measurement of the kinetics implies more efficient experimental conditions: sensitive, high resolution, exact, repeatable, rapid and low cost SOP.

At this level of experiments preparation, the basic problem is of metrology. The above mentioned aspects of morphology assert that the good metrology is not is sufficient condition for reliable results. The chemical structure of a system does not univocally define the final morphology. Metals and metallic alloys are commonly known examples.

What exactly do means kinetics? A transformation process starts and finishes in a finite period of time in more or less controlled conditions. In that period of time the variation of a parameter can be measured in good metrology. This parameter is chosen as a suitable and most representative quantity called as the **response function (RF)** of the measuring system. Most of the experimenters know that the "time-conversion" of a such RF may be one of the two types presented in Figure 1.

The two types correspond to the integral forms fro which the maximum value of kinetic rate =  $\max (dRF/dt) = MKR$ , occurs at the starting point (Figure 1A) and at the induction period of time (IT)(Figure 1B).



**Figure 1.** Two representative types of the integral forms For RF time-conversion and their main EV.

In view to define the behaviour of a test-specimen in the frame of the measuring system, we don't need all of RF time-conversion, but a significant quantity called as **eigenvalue (EV)** symbolized by  $\theta$ . Experimenters, especially in chemical kinetics, usually consider as EV the following quantities: MKR, IT,  $t_{1/2}$ , (the half time),  $t_f$ , (the time period at which RF reaches the final equilibrium value, RFE), RFE, etc.

In view to effectively measure the transformation process, we must trigger it in accurate conditions. Practically, the measuring system is prepared in all respect, so the test-specimen does not react (the measuring parameter has the baseline value, RFBL) and by a standard perturbation in a driving potential (generally symbolized as U) the process is triggered.

We may conclude that the measuring system relative to which the behaviour of a test-specimen we intend to define, mainly consists in: SOP,  $\theta$  and U.

#### 4.COMPOSITE STRUCTURE OF THE TRANSFORMING SYSTEM

SOP, including the experimental conditions, is imposed for reliable results and we will detect on practical examples what exactly this means. In particular case of solubility tests using WOS, SOP must standardize also WOS morphology. We already have recognized its composite structure, but this notion is classically defined by direct structural methods.

By addition of the test-specimen, two molecular species separate, namely: one with predominant hydrophile behaviour (MW) and another one with lipophile behaviour (MO). We must observe that the test-specimen becomes by transforming as composite. The value of the two components denoted as MW and MO, directly measures this composite structure and depends on the SOP, so we are able to define again this notion by kinetic behaviour of the test-specimen.

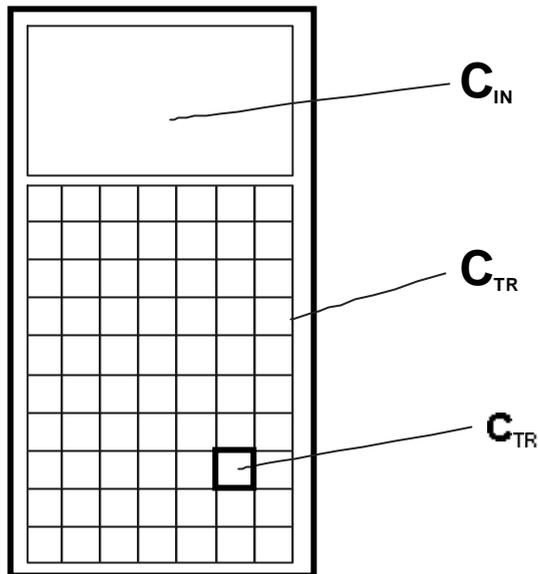
We also must observe, as a general rule, that not all of the test-specimen participates to the transforming process. For the particular case of WOS solubility, MW and MO represent the transforming (Ctr) and the inert (Cin) components, respectively.

We must observe further that: Ctr is a measure for the process amplitude and both components are interrelated. For instance, we may consider a RF proportional either with Ctr or Cin. On the other hand, these two quantities define again the notion of the mass as expressed in units of EV in standard conditions expressed by SOP.

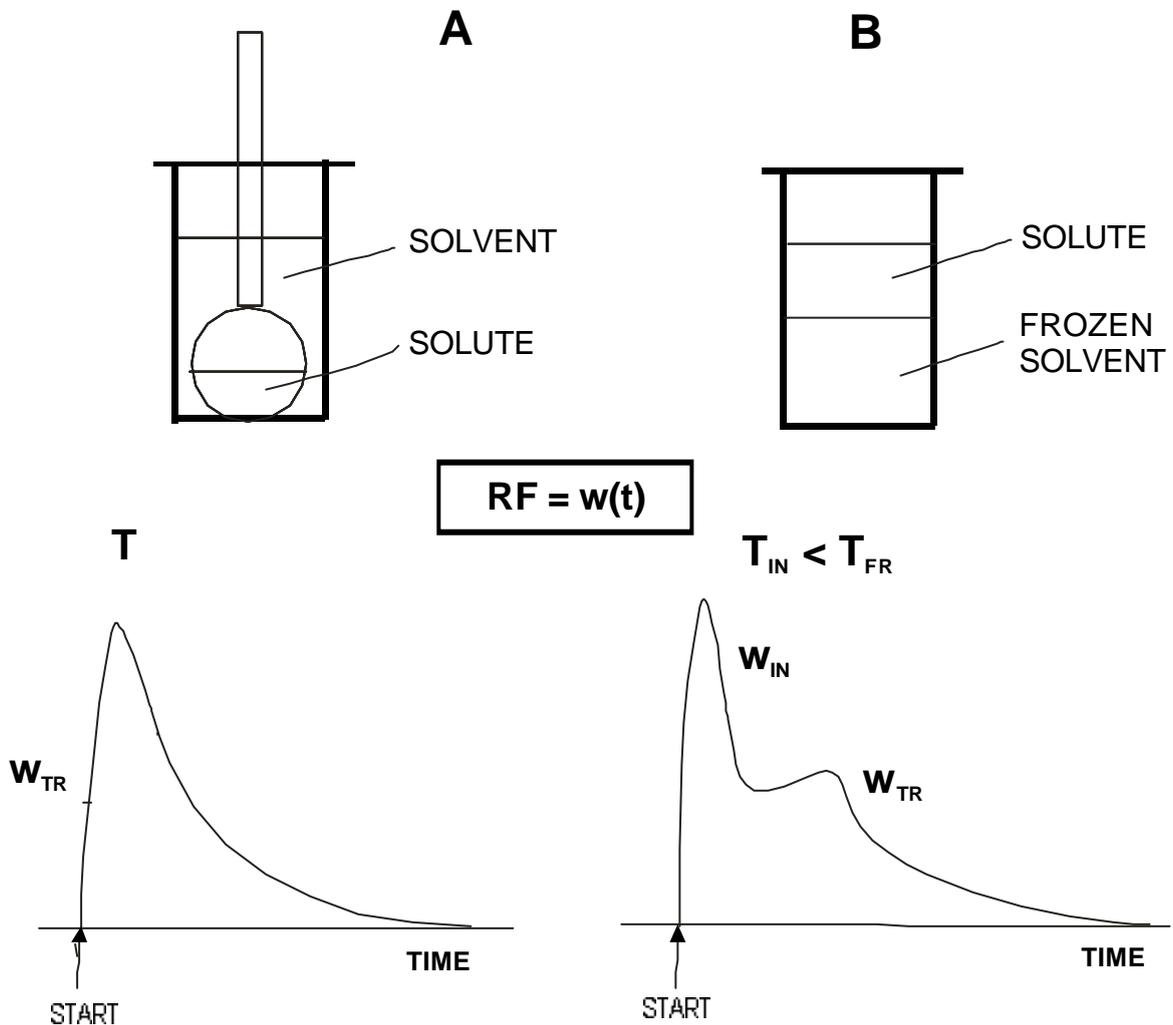
It appears as necessary condition to include in SOP the dimensions of the test-specimen, so the process amplitude results directly in units of RF. Another important reason, generally recognized by the experimenters, is the fact that the **nature** of the transforming process depends on the dimensions of the all components in the measuring system including also the test-specimen. As a result of a long experience in material testing, the more correct manner to standardize the dimensions of the test-specimen is by its volume and shape not by weight. Further examples will better show this aspect.

The kinetic entity (ctr) responsible for the transforming process is the smallest part of Ctr and it is important to observe that this could be a submolecular, molecular and/or supramolecular species.

The standard test-specimen can be schematically represented as in Figure 2. The graphic representation is useful for many practical cases to understand the nature of the transforming processes.



**Figure 2.** Schematically drawn of the composite structure of the test specimen normalized in volume and shape.



**Figure 3.** Isothermal differential calorimetric measuring systems used for solution behaviour (see the text).

## 5. RELATIVISTIC EFFECTS

The solution process may be imagined by the measuring system with WOS as solvent. It is interesting to consider the two extreme cases of WOS concentration. For water as the solvent, C<sub>TR</sub> is represented only by MW, so MO does not separate by C<sub>IN</sub>. The symmetric case of 1-octanol as the solvent has C<sub>TR</sub> = MO and C<sub>IN</sub> = MW. For an intermediate case of WOS, the two components appear also as intermediate combination. We may observe that the process amplitude appears as a relativistic effect in respect to the frame system of the measuring system.

To be more specific, we consider an isothermal and differential calorimetric measuring system for which  $RF = w(t)$  is the instant caloric flow and  $U =$  temperature. We may imagine the solution experiments in two different SOP, with specific difficulties, but having similar final products (not identical !)(Figure 3):

- (i) the calorimetric cell is prepared at the measuring temperature  $T$  by separation of WOS by the test-specimen by using a glass bubble (Figure 3A). The solution process is triggered by cracking this bubble.
- (ii) The calorimetric cell is prepared at an initial temperature,  $T_{IN}$ , below the freezing point,  $T_{FR}$ , of WOS or of the test-specimen, so that they do not interact (Figure 3B). The solution process is triggered by transferring the cell to the measuring temperature,  $T > T_{FR}$  at which the calorimetric measuring system is already prepared.

The respective time conversion of  $w(t)$  for the two cases (Figure 3) allows to evidence the relativistic effect. In the first case, only the heat flow,  $w_{TR}$ , associated with the C<sub>TR</sub> appears, while in the second case, both components are revealed by the respective heat flows (we have considered the solution process as endothermal). For practical application we may consider as EV in both cases  $\theta = t_M$  – the period of time for which MKR is reached.

We must observe that  $w_{TR}$  appears as a delayed process in both cases relative to  $w_{IN}$  occurring instantly with the process triggering. This means that the C<sub>IN</sub> is located in the same time frame as the measuring system (laboratory frame), while C<sub>TR</sub> has a proper time-frame. We may add that if the  $w_{IN}$  is always as endothermal (in the same measuring system),  $w_{TR}$  could be in particular cases endothermal or exothermal. This is discussed in more detail a little further.

We must mention that **High Resolution Mixing Calorimetry (HRMC)** can be and it has already applied to practically unlimited cases of transforming processes as a highly efficient tool in evidencing the nature, amplitude and many relativistic aspects directly connected to structure.

## 6. AFFINE RELATIONSHIPS

We must observe that the stepwise variation of  $U$  from  $U_{IN}$  to the measuring value  $U$ , has an intermediary value  $U_0$  called as the threshold value ( $U_{IN} \leq U_0 < U$  or  $U_{IN} \geq U > U_0$ ), so that the transforming process is practically inhibited in the closed range  $[U_{IN}, U_0]$ . In the above presented cases, the freezing point of solvent and/or of the test-specimen, represents this threshold temperature.

It is important to note that the value of  $U_0$  cannot be directly measured in these measuring systems, because according to its definition at this value no process occurs.

In a correct SOP for which a series of identical standard test-specimens are considered, the following UNIVERSAL kinetic eqn exists:

$$\ln \theta = \ln |U - U_0| + M \quad (1).$$

Due by its linear form this relationship is called as affine relationship. Its main assignment consists in the fact that the basic experimental values ( $\theta$ ,  $U$ ) obtained for identical test-specimens, allow to evaluate the **first affine** or **ontogenic** parameters ( $N$ ,  $M$ ,  $U_0$ ) defining the behaviour of the tested sample relative to the applied SOP.

It appears more clear that  $U_0$  results as a particular value relative to the measuring system. For instance, the freezing point of a liquid may results as significantly different values in the two different measuring systems (see Table 1).

**Table 1.** Two measuring systems defining the freezing point of liquid samples.

Measuring system →	Isothermal flow kinetics (viscometry)	Isothermal HRMC (see Figure 3)
$\theta$	Kinematic/dynamic viscosity	$t_M$
$U$	temperature	temperature

## 7. PYRAMIDAL STRUCTURE OF TOPOENERGETIC DATABANKS

By considering a series of samples tested in the same SOP, having the same process nature, but with different amplitude, their associated ontogenic parameters are interrelated in a second-affine relationship:

$$N = n_1 * M + m \quad (2),$$

where the **second-affine** or **first phylogenetic parameters** ( $n_1$ ,  $m_1$ ) define in fact the nature of the common process triggered in the same SOP for the tested samples. For a significant number of samples tested in the same SOP according to above mentioned topoenergetic requirements, we may obtain higher phylogenies, so it is easy to observe the pyramidal structure of the obtained databank: at the basis are the BED and towards the pyramid's top are placed phylogenetic parameters with progressively increasing phylogeny.

## 8. GOOD METROLOGY

We have already pointed out that pairs of BED values ( $\theta$ ,  $U$ ) are only the parameters measured in the imposed SOP for which is necessary a good metrology. We must note that the affine relationships proper to different SOP make things much easier for reproduce and to calibrate them in different laboratories. For instance, the same SOP considered in view to create databanks, but there are inherent differences in "device constants", experimentally it has been established also affine relationships (or linear scaling laws) of the type:

$$\theta_1 = a * \theta_2 + b \quad (3),$$

where  $\theta_1$ ,  $\theta_2$  are EV associated to the two SOP (differing even by one respect each other), but obtained for the same sample.

Good metrology appears to be resolved at once by calibration of the process nature and using certified reference samples.

### 9. PORCESS POLARITY

The above mentioned calorimetric measuring system (**HRMC**) (Figure 3), allowed to distinguish cases for which  $w_{TR}$  and  $w_{IN}$  are of the same or of opposite signs. These two situations will correspond to the cases with positive and negative activation energy (E), respectively, in Arrhenius representation of BED. We may assign by convention to the two cases different polarity of the transforming process. This proposed convention is based on a long experience and could be shortly sketched as in Table 2 and verified on solubility behaviour of following series:

Solute series: XY (X: Na, K, NH<sub>4</sub>; Y: Cl, Br, I, CNS)

Solvent series: formamide; N-methyl formamide; N,N'-dimethyl formamide

SOP:  $\theta$  = isothermal equilibrium solute concentration ; U = temperature

BED are taken from "Solubility Data Series", B.Scrosati and C.A.Vincent, Editors and Evaluators, Pergamon Press, vol.11, Oxford, series IUPAC, 1980.

Topoenergetic databanks in both UNIVERSAL and Arrhenius representations are presented recently (Gh.Dragan, "Upon some topoenergetic aspects of solubility behaviour", Vth International Symposium on Solubility Phenomena, N.S.Kurnakov Institute of General and Inorganic Chemistry, July 8-10, 1992, Moscow, Russia) and will be detailed in a separate paper of this Bulletin with structural aspects.

**Table 2.** Conventional definition of polarity of transformation process (associated with solution behaviour).

SIGN( $w_{tr} \cdot w_{in}$ )	SIGN(S)	ARRHENIUS			UNIVERSAL			POLARITY
		SIGN(E)	SIGN (n1)	SIGN (E*n1)	SIGN (N)	SIGN (n1)	SIGN (N*n1)	
+	-	+	+	+	+	-	-	+
-	+	-	+	-	-	-	+	-

$S = \delta[\text{solute}]_{eq} / \delta T$ ;  $w_{IN}$  is always as endothermal.