

Isopiestic Density Law of Actinide Nitrates Applied to Criticality Calculations

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Up to now, criticality safety experts used density laws fitted on experimental data and applied them in and outside the measurement range. Depending on the case, such an approach could be wrong for nitrate solutions. Seven components are concerned: $\text{UO}_2(\text{NO}_3)_2$, $\text{U}(\text{NO}_3)_4$, $\text{Pu}(\text{NO}_3)_4$, $\text{Pu}(\text{NO}_3)_3$, $\text{Th}(\text{NO}_3)_4$, $\text{Am}(\text{NO}_3)_3$ and HNO_3 . To get rid of this problem, a new methodology based on the thermodynamic concept of binary electrolytes solutions mixtures at constant water activity, so called “isopiestic” solutions, has been developed by IRSN to calculate the nitrate solutions density. This article shortly presents the theoretical aspects of the method, its qualification using benchmarks and its implementation in I.R.S.N. graphical user interface.

KEYWORDS: criticality, actinide nitrate binary data, constant water activity.

1 Introduction: Density Laws used in Criticality

Criticality calculations need, as input data, the atomic densities of fissile mixtures. Density laws are used to calculate them in solution mixtures and derive the water content, which rules the reactivity. They are relationships between mixture density and actinide concentration, acidity and temperature: $\rho = f(C(X), H^+, T)$ (0)

1.1 Empirical Laws

Seven main electrolytes of actinides in nitric acid solutions (HNO_3 , $\text{UO}_2(\text{NO}_3)_2$, $\text{Pu}(\text{NO}_3)_4$, $\text{Th}(\text{NO}_3)_4$, $\text{Pu}(\text{NO}_3)_3$, $\text{Am}(\text{NO}_3)_3$ and $\text{U}(\text{NO}_3)_4$) are used in the fuel cycle manufacturing and the spent fuel reprocessing. Many density laws have been published¹⁾. Most of them are strictly empirical: many experimenters have proposed mathematical fittings of experimental data, based on various polynomial expressions: amongst them, the so called uranyl nitrate Leroy & Jouan and plutonium nitrate ARH-600 laws. These laws have been selected in the French criticality practice. Nevertheless, it must be noticed that they are first order polynomials; thus the density depends linearly on the actinide concentration. When used at high concentration levels, these polynomials do not give a good estimate of the density. Thus, the plutonium nitrate density law published in the ARH-600 guide, by underestimating the solution density (i.e. water content), entails underestimates of the k_{eff} calculated for concentrated solution (around 200 g/L - geometry optimum).

1.2 Isopiestic Law – Theoretical Considerations

Therefore, since 2000, a new method based on a thermodynamic approach has been introduced in CIGALES V2.0²⁾ code, the graphical user interface that calculates the atom densities of nuclides. This approach

uses the thesis works done at CEA/INSTN^b since 1981 for the concentrated solutions.

These works find their roots in 1936 when Zdanovski studied the behaviour of binary solutions mixtures. The mixtures of several solutions have the same water activity as the initial solutions provided that no specific interaction between the dissolved species exists. Such mixtures are called simple solutions. An equivalent behaviour has been pointed out in the case of mixtures of “non electrolytes”. It is known under the denomination of Zdanovski-Stokes-Robinson behaviour (Z.S.R.)³⁾.

The Z.S.R. rule can be expressed as follows (see also the nomenclature at the end of the paper):

$$\sum \frac{m(X_i)}{m^{bi}(X_i)} = 1, \quad a_w = \text{constant} \quad (1)$$

This formula only expresses the mass conservation when mixing, at constant water activity, a_w . Of course it fits to any mixture, without any restriction on a_w . Ryazanov⁴⁾ showed that the volumes of several binary solutions having the same water activity could be added, the resulting mixture having the following V_{mix} and ρ_{mix} .

$$V_{\text{mix}} = \sum \frac{m(X_i)}{m^{bi}(X_i)} \times V^{bi}(X_i) \text{ then,} \quad (2)$$

$$\rho_{\text{mix}} = \sum \frac{C(X_i)}{C_{bi}(X_i)} \times \rho_{bi}(X_i) \quad (3)$$

A bibliographical review of the available binary data for many ternary systems shows that a few systems follow strictly the Z.S.R. rule; as a matter of fact, in 1973, Chen, Lenzi & al⁵⁾, in a compilation of data coming from literature, presented the behaviour of approximately hundred ternary aqueous systems with regard to the simple solutions concept; this study showed that, even if only a few systems strictly followed the Z.S.R. rule, this rule is a very good approximation for the other tested systems. One should pay attention to the following points:

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^b C.E.A./I.N.S.T.N.: Commissariat à l’Energie Atomique/Institut National des Sciences et Techniques Nucléaires

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- the discrepancies are all the weaker as the physicochemical properties of the present components are similar.
- the discrepancies grow with the concentrations increasing that is to say with the water activity decreasing.

On the basis of the “Z.S.R. behaviour”. Dannus⁶¹ gave the bases of a methodology to provide a data set (concentration, water activity, activity coefficient) of “fictitious” binary solutions $\text{Pu}(\text{NO}_3)_4/\text{H}_2\text{O}$ from 1991.

In 2000, Charrin’s works⁷¹ led to data of fictitious binary solutions of electrolytes such as $\text{Pu}(\text{NO}_3)_4$ and $\text{U}(\text{NO}_3)_4$ on a large concentration range. At the same time, being at the origin of a new experimental protocol. Charrin pointed out the water activity area for which the “Z.S.R. behaviour” was strictly followed for mixtures such as $\text{Pu}(\text{NO}_3)_4/\text{HNO}_3/\text{H}_2\text{O}$ and $\text{U}(\text{NO}_3)_4/\text{HNO}_3/\text{H}_2\text{O}$. A part of his work consisted in adding the variable “density” to other variables such as concentration, water activity and activity coefficient.

These works enabled IRSN to implement the “isopiestic” density law in the CIGALES V2.0 code.

The main results about the “isopiestic” density law are dealt with in⁸¹ where the theoretical aspects and the implementation in CIGALES V2.0 are described in details. Moreover, it should be added that the theoretical aspects of the method had already been presented at the ICNC’99⁹¹.

1.3 Restrictions

Two types of restrictions with regard to the use of the “isopiestic” density law can be quoted:

- (1) those linked to the binary data (range of values and temperature: 25°C):

for the studied electrolytes, the range of binary data are:

- $\text{UO}_2(\text{NO}_3)_2$: $a_w \in [0.5934; 1]$, $c(X) \in [885; 0]$.
- $\text{Th}(\text{NO}_3)_4$: $a_w \in [0.57; 1]$, $c(X) \in [631; 0]$.
- $\text{Pu}(\text{NO}_3)_4$: $a_w \in [0.677; 1]$, $c(X) \in [556; 0]$.
- $\text{U}(\text{NO}_3)_4$: $a_w \in [0.699; 1]$, $c(X) \in [503; 0]$.

The binary data range of HNO_3 at 25°C is far wider: it extends from 1 to 0.23 for a_w , which corresponds to a concentration range from 0 to 14 mol/L.

In the case of americium nitrate and plutonium (III) nitrate, as binary data are not available for these electrolytes, and as their physicochemical properties are close to that of neodymium, it has been proposed to use neodymium binary data and correct the density.

- (2) those linked to the physicochemical behaviour of the mixture:

indeed, the relationship developed by Ryazanov and Vdovenko is derived from the Z.S.R. rule. As a consequence, strictly speaking, this relationship is thermodynamically exact only if the mixture follows the “Z.S.R. behaviour”. Such a behaviour cannot be true on the whole concentration range (see § 1.2). Generally, the lower the water activity, the higher the deviation to the “Z.S.R. behaviour”. In the case of

ternary mixtures $\text{Pu}(\text{NO}_3)_4$ ¹⁰¹ or $\text{Th}(\text{NO}_3)_4$ ¹¹¹ with HNO_3 . Charrin & al pointed out the water activity values beyond which a noticeable deviation to the “Z.S.R. behaviour” was observed in terms of water activity.

Nevertheless, these authors also showed that, in the range “beyond “Z.S.R. behaviour”, the calculation of the density of ternary solutions $\text{Pu}(\text{NO}_3)_4$ or $\text{Th}(\text{NO}_3)_4/\text{HNO}_3$ with regard to the “isopiestic” density law would lead to low differences (< 0.6%) in comparison with the density experimental values. Moreover, these differences are less important than that encountered in the “Z.S.R. behaviour” area. This result has also been confirmed on quaternary mixtures $\text{UO}_2(\text{NO}_3)_2/\text{Pu}(\text{NO}_3)_4/\text{HNO}_3/\text{H}_2\text{O}$ ¹²¹. As a consequence, and even if the “Z.S.R. behaviour” is not strictly followed by all the considered mixtures, the “isopiestic” density law is a good means to calculate the mixtures density of actinide nitrates, nitric acid and water,

- (3) those linked to the electrolyte solubility limit knowledge:

up to now, usual criticality computations had never taken into account the solubility limits of the electrolytes in solution. In the present case, it has been decided to take it into account for the two following ternary solutions^c:

- $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$.
- $\text{Pu}(\text{NO}_3)_4/\text{HNO}_3/\text{H}_2\text{O}$.

It means that, as soon as the solubility limit of the electrolyte is reached, the solution is saturated and a crystal precipitates: a two phased system is formed (crystal + saturated solution) (see Figure 1).

The calculation results given outside a specified water activity range in terms of densities can be in good agreement with the experimental measurements (see § 1.3). Therefore, the binary data of the electrolytes have been extended beyond the activity range following the Z.S.R. rule to cover the major part of the concentration range met in the spent fuel reprocessing, and even to reach the solubility limit of the electrolyte.

One disposes of ternary diagrams giving the solubility of $\text{UO}_2(\text{NO}_3)_2$ and $\text{Pu}(\text{NO}_3)_4$ in an acidic medium. Thus, in CIGALES V2.0, it has been decided to extend the law range beyond the solubility of these electrolytes in the ternary mixture by using a volume addition law for the two ternary solutions.

For other electrolytes and for the n-ary solutions ($n > 3$), the “isopiestic” method has not been extended

^c Density of the crystals

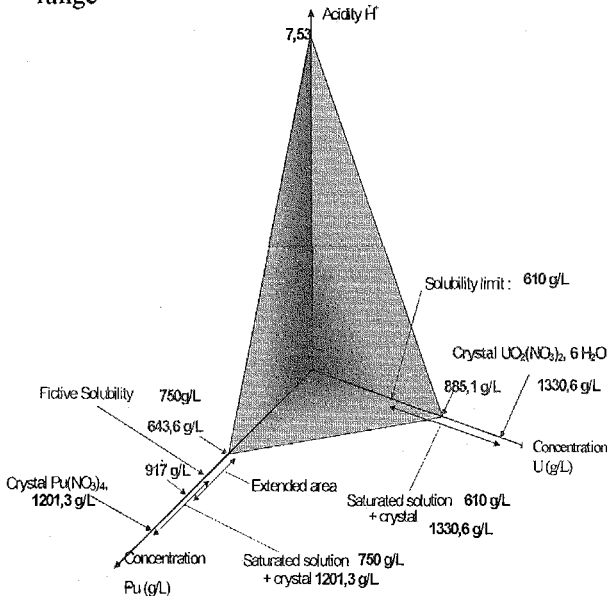
$\text{UO}_2(\text{NO}_3)_2$, 6 H_2O : 2.807 g/cm³ (uranium in natural abundance),

$c(\text{U}) = 1330$ g/L,

$\text{Pu}(\text{NO}_3)_4$, 5 H_2O : 2.9 g/cm³ (100 % ²³⁹Pu) $c(\text{Pu}) = 1201$ g/L.

^d International Handbook of Evaluated Criticality Safety Benchmark Experiments

over the solubility limits of the electrolytes. The method is only applied on the binary data validity range



activity limit: 0.5934,
 plutonium: 643.6 g/L ↔ 2.6919 mol/L,
 uranium: 885.1 g/L ↔ 3.71847 mol/L

Fig.1 Binary data field of the Pu(NO₃)₄/UO₂(NO₃)₂/HNO₃/H₂O solution

2 Qualification of the Method using Benchmarks

The use of benchmarks is really an original means for qualification of the method. On that purpose, 40 benchmarks provided by the ICSBEP^d handbook are used. Using the ICSBEP nomenclature, they can be divided into four categories:

- PU-SOL-THERM.001, for the solutions of Pu(NO₃)₄ performed in 1966 at the Hanford Laboratory,
- LEU-SOL-THERM.004 and 016, for the solutions of UO₂(NO₃)₂, at a low ²³⁵U enrichment performed by JAERI in STACY in 1995 and 1997,
- HEU-SOL-THERM.001, for the solutions of UO₂(NO₃)₂ at a high ²³⁵U enrichment performed at Rocky Flats in 1978,
- MIX-SOL-THERM.003, for the mixed solutions of Pu(NO₃)₄ and UO₂(NO₃)₂ performed in 1970 by AWRE at Aldermaston (UK).

The only parameter that differs from one density law to another is the water concentration, the k_{eff} being very sensitive to that parameter.

These benchmark configurations have been evaluated using atom densities taken from analysis data provided by ICSBEP or calculated using density laws ("isopiestic" method or the Leroy & Jouan/ARH-600 density law¹²). The solution densities calculated with the "isopiestic" law are in good agreement with those provided by the benchmarks (difference lower than 1%). The evolution of

the k_{eff} in accordance with the uranium or plutonium concentration is presented on Figures 2, 3 and 4.

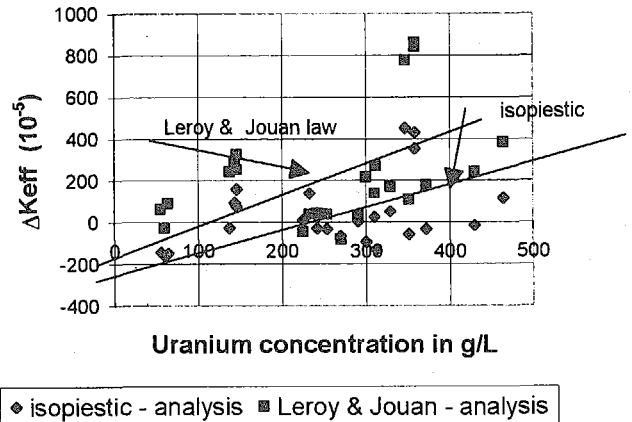


Fig.2 qualification of uranyl nitrate - HEU-SOL-THERM.001 and LEU-SOL-THERM.004 and 016

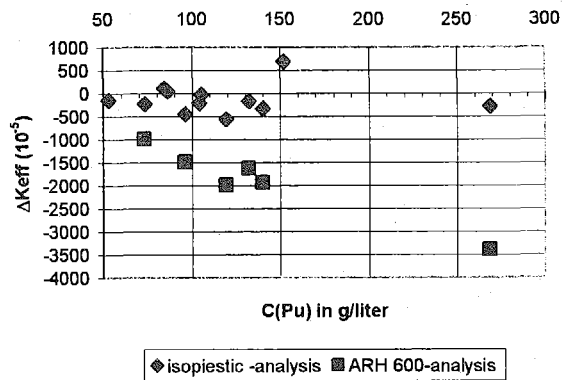


Fig.3 qualification of plutonium nitrate - PU-SOL-THERM.001

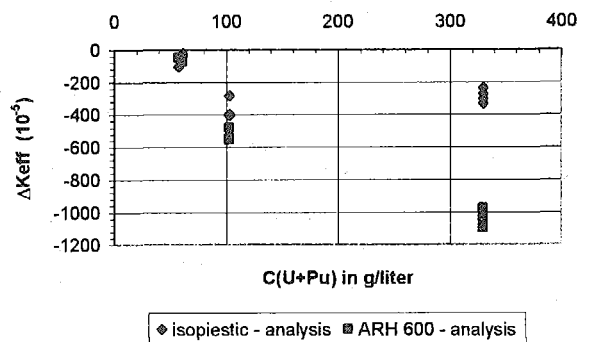


Fig.4 qualification of mixed (U+Pu) nitrate - MIX-SOL-THERM.003

The k_{eff} values can be roughly split into two categories :

- uranium solutions for which there is no bias, k_{eff} differences (Δk_{eff} (calculation-benchmark)) between the calculation and the benchmark being randomly distributed around zero,
- plutonium solutions and mixed solutions uranium + plutonium for which there is a slight negative bias (Δk_{eff} (calculation-benchmark) < 0.2%).

Moreover, the use of the “isopiestic” density law corrected the 3.4 % underestimation of the k_{eff} due to the use of the ARH-600 density law, for the plutonium solutions and the 1 % overestimation of the k_{eff} due to the use of the Leroy & Jouan density law, for the uranium solutions.

As the qualification results are better, the “isopiestic” density law has been implemented in CIGALES V2.0, in the place of the former laws.

Yet, it should be reminded that the validation work is limited to the solubility range of the electrolytes and to the validity area of the Z.S.R. rule. Without experimental data, it cannot be applied to americium and thorium solutions.

3 Implementation of the method in CIGALES V2.0

The method used to compute the water densities in CIGALES V2.0 is an iterative method. The flowsheet is described on Figure 7. It can be split into several cases depending on the input data and on the electrolyte concentration:

- the electrolyte concentration is given as input data;
- the moderation ratio is given as input data;
- the solubility limit has been reached.

The main step of the method consists in determining the binary solutions having the same water activity as the mixture with the Z.S.R. formula. Then, formula (3) is applied and the water density is known. The different steps are summarized on Figure 7.

4 Consequences on Physical Parameters

The influence of the model can be judged in particular on fissile medium parameters such as the molar volume of the electrolyte in solution and criticality reactivity (material buckling).

4.1 Fissile Medium Moderation - Electrolyte Molar Volume

It had been assumed, in § 1.1, that, for the nitrate density law used up to now, the molar volume of an electrolyte in solution did not depend on the concentration of this electrolyte in solution. This hypothesis allowed to linearly extend density versus electrolyte concentration.

For instance, the density of a fictitious binary solution of plutonium nitrate ($\text{Pu}(\text{NO}_3)_4$) was determined using a first order polynomial expression. Hence, the molar volume is constant. A mathematical extrapolation of the density law not based on a thermodynamic approach is wrong for high electrolyte concentrations. Anyway, the molar volume of the electrolyte depends on the concentration of the electrolyte.

The molar volume of an electrolyte V in a binary solution with $C^{bi}(X_i)$ moles of electrolyte is obtained by the hereafter formula; it is obviously strongly dependant on $C^{bi}(X_i)$.

As shown on Figure 5, one can see that the molar volume of $\text{Pu}(\text{NO}_3)_4$ in solution calculated with formula (4) increases with the concentration of plutonium; moreover, the true molar volume derived from relation (4) is lower than the one achieved with the ARH – 600 law formerly used by I.R.S.N.

It can be derived that the approach based on formula (4) leads to a reactivity value higher than the one based on the ARH – 600 law, which has really been verified on the criticality benchmarks.

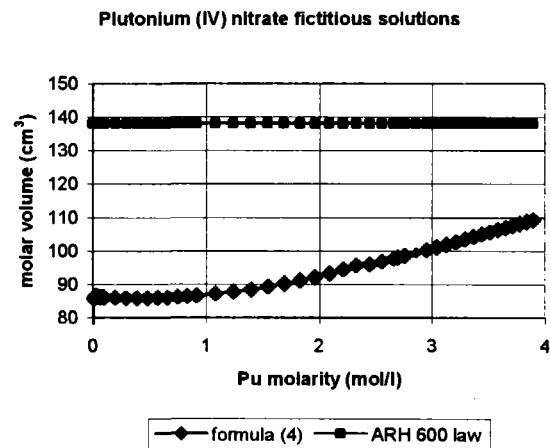


Fig.5 variation of the molar volume of the $\text{Pu}(\text{NO}_3)_4$ along with concentration

$$V = \frac{C^{bi}(X_i) \times M(\text{electrolyte}) + 1000 \times (\rho_{\text{H}_2\text{O}} - \rho_{bi}(X_i))}{C^{bi}(X_i) \times \rho_{\text{H}_2\text{O}}} \quad (4)$$

The largest k_{eff} difference (Δk_{eff}) is evaluated to around $3400 \cdot 10^{-5}$. The noticeable difference between the molar volumes given by the two approaches has no consequence on the water concentration and on the k_{eff} value for low Pu concentrations but for higher Pu concentrations, it accounts for the difference on the k_{eff} value, as the difference of the water concentrations between the two approaches increases in keeping with the Pu concentration. The opposite trend is observed for uranyl nitrate solutions.

4.2 Criticality Reactivity Parameters – Material Buckling

The knowledge of the molar volume of the electrolyte is not enough to appreciate the conservatism of a density law. The material buckling is the physical parameter linked to the reactivity of the medium.

This physical parameter stands for the neutronic leakages within the fissile medium, displayed on Figure 5 for U & Pu solutions.

Curves on Figure 6 show the material buckling evolution versus the moderation ratio for two binary solutions (electrolyte + water) of uranyl nitrate and plutonium nitrate.

For uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2$) and plutonium nitrate ($\text{Pu}(\text{NO}_3)_4$) water solutions, the crystal precipitates and coexists with a homogenized solution of saturated uranyl

nitrate or plutonium nitrate if $H/U < 40$ or $H/Pu < 35$, also depending on acidity.

We can notice that for the uranyl nitrate and the plutonium nitrate solutions, the approach based on the use of the physicochemical binary data gives reactivity values slightly below the Leroy & Jouan law (respectively over the ARH-600 law).

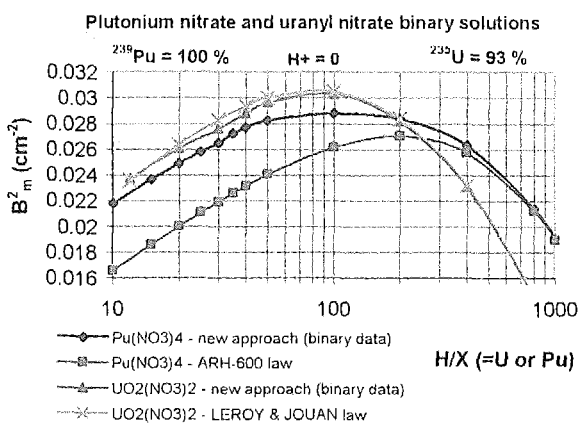


Fig.6 binary solution uranyl nitrate/H₂O: variation of B_m^2

4.3 Criticality Applications: Minimum Critical Values

Minimum critical values (MCV) are of great importance in criticality: they give the maximum parameter (radius, thickness) value possible without any risk of criticality accident. This item is dealt with in^[2], which also provides a data comparison of various MCV from different CRISTAL routes. The standard route (Apollo2 S8 P3, 20 energy groups from CEA 93 library) is slightly conservative.

5 Conclusion

Binary data available for nitrate solutions made it possible to build up a new density law using an iterative method based on a thermodynamic approach called "isopiestic method". This method is very general and was compared with a volume addition law of several binary solutions (one electrolyte + water) having the same water activity, in which the electrolytes have no specific interaction one with the other (Z.S.R. rule).

At least five nitrates in an acidic medium follow more or less the Z.S.R. rule; they are: HNO_3 , $UO_2(NO_3)_2$, $U(NO_3)_4$, $Pu(NO_3)_4$, $Th(NO_3)_4$.

In addition to that, for the two ternary solutions $UO_2(NO_3)_2/HNO_3/H_2O$ and $Pu(NO_3)_4/HNO_3/H_2O$, the method based on the Z.S.R. rule has been replaced by a volume additive law beyond the solubility limit of the electrolytes.

The conclusions of the qualification results are as follows:

- this law corrects the observed 3.4 % underestimation of the k_{eff} of the ARH-600 density law (plutonium solutions);

- it decreases slightly the observed 1 % overestimation of the k_{eff} of the Leroy & Jouan density law (uranium solutions);
- the new nitrate density law shows no systematic discrepancy, applied to benchmark evaluation, for the uranium solutions and a slight negative bias for plutonium and uranium-plutonium solutions.

For the moment, the method is conservatively limited by the temperature, at which the binary data are measured (25°C). All the calculations are done at 25°C and it proves to be conservative for electrolytes at higher temperatures^e.

Given that it provides an accurate estimation of the mixture density and improves the results in comparison with the "classical" laws, the new nitrate density law has been implemented in the CIGALES V2.0 code, to calculate the atomic densities by an iterative method. New minimum critical values have been calculated for uranyl nitrate and plutonium nitrate solutions at various ^{235}U enrichments, plutonium isotopic vectors and reflection conditions.

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^e For specific concentration values (< 20 g/l), it has been shown by Yanamoto & al that a temperature increase can lead to an increase in k_{eff} value; it is known as being a Pu-temperature effect.

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Nitrate dilution laws
Determination of C(X) or H/X
Calculation of ρ

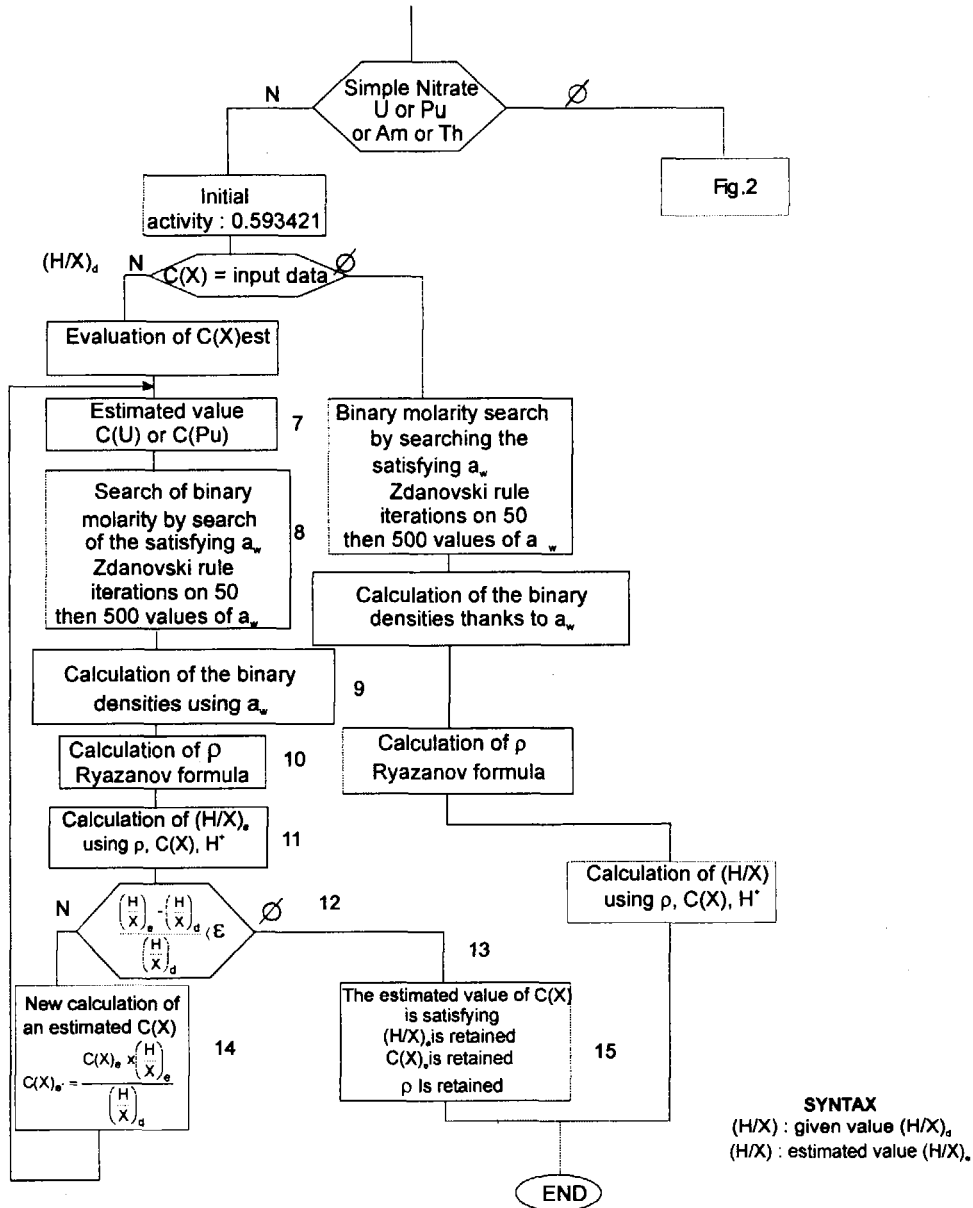


Fig.7 Implementation of the iterative method in CIGALES V2.0

Nomenclature

- 1) X = sum of electrolytes X_i
- 2) XNIT = electrolyte (HNO_3 , $\text{Pu}(\text{NO}_3)_4$, $\text{UO}_2(\text{NO}_3)_2$...).
- 3) X_i = positive ion of the electrolyte : Pu^{4+} , U^{6+} , ...
- 4) $V(\text{XNIT})$: molar volume of the nitrate compound (i.e. $\text{Pu}(\text{NO}_3)_4$, ...).
- 5) $M(\text{XNIT})$: molar mass of the nitrate compound.
- 6) $C(X_i)$: concentration of component i in the mixture (mol/L).
- 7) $c(X_i)$: concentration of component i in the mixture (g/L).
- 8) $m(X_i)$: molality of component i in the mixture (mol/kg of water).

- 9) $C_{bi}(X_i)$: concentration of component i in the binary solution at the same a_w as the mixture (mol/L).
- 10) $c_{bi}(X_i)$: concentration of component i in the binary solution at the same a_w as the mixture (g/L).
- 11) V_{mix} : mixture volume (cm^3).
- 12) $V_{bi}(X_i)$: volume of the binary solution at the same a_w as the mixture (cm^3) containing X_i .
- 13) ρ_{mix} : mixture density (g/cm^3).
- 14) $\rho_{bi}(X_i)$: density of the binary solution at the same a_w as the mixture (g/cm^3) containing X_i .
- 15) $M(X_i)$: molecular weight of component i (g/mol).