



## Solid + liquid equilibria and molecular structure studies of binary mixtures for nitrate ester's stabilizers: Measurement and modeling



Salim Chelouche<sup>a,\*</sup>, Djalal Trache<sup>a,\*</sup>, Catarina M.S.S. Neves<sup>b</sup>, Simão P. Pinho<sup>c,d</sup>,  
Kamel Khimeche<sup>a</sup>, Mokhtar Benziane<sup>e</sup>

<sup>a</sup> UER Procédés Energétiques, Ecole Militaire Polytechnique, EMP, BP 17 Bordj-El-Bahri, Algiers, Algeria

<sup>b</sup> CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

<sup>c</sup> Associate Laboratory LSRE-LCM, Departamento de Tecnologia Química e Biológica, Instituto Politécnico de Bragança, Bragança, Portugal

<sup>d</sup> Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

<sup>e</sup> Ecole Supérieure du Matériel ESM, BP 188 Beau-Lieu, Algiers, Algeria

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### ABSTRACT

Solid-liquid equilibria (SLE) data for two binary organic mixtures of N-(2-methoxyethyl)-p-nitroaniline + N-ethyl-4-nitroaniline (S1) and N-(2-ethanol)-p-nitroaniline + N-ethyl-4-nitroaniline (S2) have been measured using differential scanning calorimeter to build the corresponding solid-liquid phase diagrams. The quality of the SLE data has been checked by consistency tests, presenting good quality factors for both systems. Simple eutectic behavior has been observed for these systems with the presence of a solid-solid transition for S2. The SLE data have been correlated by means of Wilson, NRTL, and UNIQUAC equations. The used models calculate the equilibrium temperatures very satisfactorily. The best modeling results were obtained using the Wilson equation with a root mean square deviation between experimental and calculated values for S1 and S2 of 1.15 and 1.99, respectively. The Wilson, NRTL, and UNIQUAC equations have also been used to compute excess thermodynamic functions viz. excess Gibbs energy, enthalpy, and entropy. The obtained results demonstrated a moderate positive deviation to ideality for S1, and a strong positive deviation for S2, unveiling the nature of the interactions between the compounds forming each mixture. In addition, microstructural studies have been carried out by FTIR, XRD and optical microscopy. Weak molecular interactions have been shown for the eutectic compositions. Jackson's roughness parameter was calculated and found to be greater than 2, suggesting the faceted morphology with irregular structures.

### 1. Introduction

Solid propellants are usually employed in military ammunition. To ensure a safe life and long storage time under adverse storage conditions with acceptable chemical, thermal, mechanical and ballistic performances, such materials should contain various chemical compounds such as stabilizers [1]. Solid propellants consisting of nitrocellulose (NC) and/or other nitrate esters (NE), are inherently chemically unstable and tend to decompose even at the normal storage conditions because of the low bonding energy (155 kJ/mol) of the nitrate ester group (CH<sub>2</sub>-O-NO<sub>2</sub>) [2–4]. They undergo slow decomposition and generate nitrogen oxides (NO<sub>x</sub>) which react with the residual moisture present in the propellant and form nitrous and nitric acids. If nothing is done to inhibit this decomposition reaction, the products act as catalysts in the decomposition of the nitrate ester, and a further decomposition reaction channel is opened which is commonly named

autocatalytic decomposition [5].

To deal with this natural slow thermal degradation, stabilizers are commonly added to the NE formulations. These substances are necessary to improve the shelf-life of propellants and to lower the risks associated with their decomposition during manufacture, storage, and use. Furthermore, the ballistic performance of propellant has been observed to change with its aging, due to physical changes in degraded propellant grains [6].

For a safe storage, stabilizers must have a relatively high melting temperature compared to that of storage. In fact, an energetic substance containing a stabilizer with a low melting point can cause its fusion. This could then cause the diffusion of the liquid within the energetic material, leading to a loss of stabilizing efficiency due to the decrease of stabilizers amount. Furthermore, the migration of the liquid after the fusion can lead to the loss of the energetic material structure integrity, thermal stability reduction, and decrease in the desired chemical,

\* Corresponding author.

E-mail addresses: [salim.chelouche@gmail.com](mailto:salim.chelouche@gmail.com) (S. Chelouche), [djalaltrache@gmail.com](mailto:djalaltrache@gmail.com) (D. Trache).

mechanical and ballistic characteristics, which can lead to self-ignition or explosion.

A wide range of chemicals has been investigated as stabilizers in propellants. However, none of these proposed substances completely fill the requirements for a safe and effective stabilizer. The research in this area is very active, seeking stabilizers that are effective and presenting fewer potential negative environmental and health impacts.

The most widely employed stabilizers are from the classes of aromatic amines (e.g. diphenylamine) and urea derivatives (Akardite-II, Akardite-III, ethyl centralite, methyl centralite) [1,2]. Some emerging substances are also being studied and evaluated (polymers, ionic liquids, organic and inorganic materials, etc.), and adding some more complexity to the search for optimum propellant formulations, stabilizers can be used either singly or in mixtures.

Numerous research studies devoted to the stabilization of nitrate esters have been conducted without sufficiently elucidating the chemical reactions that can occur between the stabilizers in the energetic material [6–9], but less attention has been paid to their thermodynamic properties and structural details. In this context, within the last ten years, several studies have been carried out by our research group with conclusive and interesting results [3,10–12].

Organic eutectics may act as blend materials, and hence their investigation for possible use in the synthesis of energetic materials is important and should be done in detail. In this paper we perform phase equilibria and microstructure studies by means of differential scanning calorimetry (DSC), Fourier transform infrared (FTIR), x-ray diffraction (XRD) and optical microscopy, for two binary mixtures of organic stabilizer's, that is N-(2-methoxyethyl)-p-nitroaniline + N-ethyl-4-nitroaniline (S1) and N-(2-ethanol)-p-nitroaniline + N-ethyl-4-nitroaniline (S2), respectively. In particular, SLE data have been correlated by means of Wilson, NRTL and UNIQUAC equations, which were also employed to compute excess thermodynamic functions, helping to understand the kind of interaction between the constituents of both systems.

## 2. Experimental and methods

### 2.1. Materials

In this work, three chemical products have been used to prepare the two binary mixtures of stabilizers. Chemical structures of studied compounds are given in Fig. 1. N-(2-methoxyethyl)-p-nitroaniline (MENA) and N-(2-ethanol)-p-nitroaniline (ENA) were synthesized and purified following the method indicated by Gibson [13]. Their purities were checked by DSC and FTIR analysis and evaluated to be greater than 98(wt.%). For the new synthesized compounds MENA and ENA,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are given as SM (Figs. S1–S4). The N-ethyl-4-nitroaniline (NENA) was supplied by Sigma-Aldrich. Its mass purity was certified by the manufacturer to be greater than 99 (wt.%) and has been used without further purification. Table 1 compiles the source and purity of the compounds.

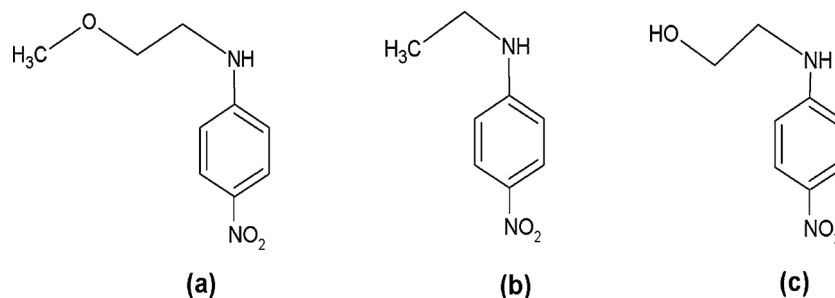


Fig. 1. Chemical structure of the studied compounds: (a) N-(2-methoxyethyl)-p-nitroaniline (MENA); (b) N-ethyl-4-nitroaniline (NENA); (c) N-(2-ethanol)-p-nitroaniline (ENA).

Their melting temperatures and fusion enthalpies were measured by differential scanning calorimetry (DSC). Table 2 lists the obtained results and their comparison with the available literature data. The knowledge of these physicochemical properties is of great importance for the determination of the activity coefficients as well as for the thermodynamic modeling. Additionally, Table 2 presents also the experimental molar volumes ( $V_M$ ,  $\text{cm}^3/\text{mol}$ ), which are calculated according to Eq. (1) [14]:

$$V_M = \frac{M}{\rho} \quad (1)$$

where  $M$  is the mass molar (g/mol) of the pure compound and  $\rho$  its density ( $\text{g}/\text{cm}^3$ ) measured at 298.15 K.

### 2.2. Apparatus and procedure

Before carrying out the DSC experiments, a series of solid binary mixtures have been first prepared. Considerable caution has been paid in preparing the samples; each mixture is placed in a separate Pyrex glass test tube and kept airtightly. The solids are slowly mixed and heated up to a temperature about 15 °C above to the melting temperature of component presenting higher melting temperature. When the first droplets of liquid appear, rapid and continuous stirring is recommended in order to ensure a good homogeneity of the binary mixture. Then, instantaneous cooling in the nitrogen liquid is carried out, in order to solidify the mixture and to keep the same homogeneous structure of the binary mixture. The resultant solid was powdered in a clean agate mortar with a little pressure as possible and dried in desiccators. The rapid cooling of molten samples ensured a uniform steric concentration of components in the mixtures and homogeneity of the final molecular blend.

The thermal properties measurements were carried out by means of a Perkin-Elmer DSC8000 (PerkinElmer, Inc., 710 Bridgeport Avenue Shelton, CT 06484-4794, USA). DSC device was calibrated with high pure indium and confirmed by analysis with zinc. The precision is within  $\pm 0.1$  K and  $\pm 2\%$  for the temperature of fusion (onset of melting peak) and the enthalpy of fusion (integral over the melting peak), respectively.

A cleaning of the measuring equipment is done ahead by infusing with nitrogen gas and then heating to a temperature of 500 °C. This procedure is carried out every time a new material series is going to be analyzed. For each measurement, 4–6 mg (Mettler H31 balance, precision  $\pm 0.0002$  g) of the sample is charged to crimped aluminum crucibles, while an empty pan of the same type is employed as a reference.

The procedure for DSC measurements is similar to those implemented in our research group for analogous mixtures [3,10,11]. It guarantees the quality and precision of the data as different heating and cooling rates, or isothermal periods, resulted in similar thermograms, without the appearance of unexpected thermal phenomena. Each sample undergoes first a heating cycle in which it is heated to a temperature higher than that of the mixture's component presenting the higher melting temperature, at a heating rate of 10 K/min, and then

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