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D1 Materials and emerging test techniques
D1 PS2 - Materials for Electrotechnical Technical Purposes and Modelling

Characterization of the liquefaction properties of fluoronitrile mixtures by a thermodynamic experimental approach

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SUMMARY

Fluoronitrile (C₄FN) based mixtures and natural origin gases like dry air are one of the alternatives to replace SF₆ in Substations in order to propose a new range of equipment with a lower environmental impact. Today, this solution is already applied in different pilot projects around the world. One of them is “Grimaud” substation in the south of France: a 145 kV Gas Insulated Substations (GIS) and the first French SF₆ free substation in service since 2018.

Lowering the CO₂ footprint of assets by reducing the use of SF₆ is a strategic goal for TSOs for the next years in order to reach Net Zero by 2050. In this direction, better and deeper knowledges on the properties of the fluoronitrile based mixtures are necessary, in particular as far as the liquefaction behaviour is concerned.

In literature, equations exist to evaluate the thermodynamic properties of gases and mixtures, like the dew point curves. However, the knowledge of fluoronitrile mixtures is still limited and these equations need to be calibrated with experimental data.

Within this scope, experimental tests have been conducted with three types of C₄FN mixtures. The tests have been performed in a climatic chamber cooling down to -40°C and a GIS compartment of about 50 L that has been equipped with different measurement sensors to monitor the temperature and the pressure of the mixture. Six different pressures for each mixture, from 5 to 10 bar abs have been investigated. The liquefaction points have been determined by decreasing the temperature until the emergence of the first drops of liquid, identified by a decreasing of the pressure with a numerical methodology.

The conducted analyses have permitted to increase the knowledge on the liquefaction point of the C₄FN mixtures and to investigate the effect of O₂ in the liquefaction behaviour. With the consistent number of data acquired during the test campaign, the experimental measurements have been fitted to obtain an equation that allows, within a certain validity range, the determination of the liquefaction points of mixtures for different molar ratios of C₄FN, O₂ and CO₂ and different pressures. The equations of state for the fluoronitrile mixtures, following the Peng-Robinson equation, have been equally determined from the experimental data. The derived equations are very interesting for the practical application of the fluoronitrile mixtures in GIS and allows the evaluation of the liquefaction points at different densities even if the molar quantity of C₄FN is changing all along the lifetime, e.g. differential permeation or refilling. It helps, for the operational point of view, to estimate the need or not for a maintenance of the GIS to recover good insulation characteristics.

KEYWORDS

Fluoronitrile, SF₆ alternative, assets, users, GIS, liquefaction, thermodynamics properties.

1. INTRODUCTION

SF₆ gas is a powerful greenhouse gas, 25 200 times stronger than CO₂ with a decay of 3200 years (approximately 80 generations). There are currently many discussions and alternatives to SF₆ rising up in the High Voltage market (both for AIS and GIS). Emissions of SF₆ gas is for some of the TSO and DSO one of the largest sources of direct greenhouse gas emissions. Many European TSO, including the author's, have published their goals to not purchase switchgears with SF₆ gas by 2026 and be SF₆ free TSO by 2050. Considering these elements and since GIS equipment have a lifetime of 50 years, SF₆ free alternative shall be implemented in the Transmission grid as soon as possible.

In the last seven years there has been a gradual change of strategy on the use of the SF₆ gas within electrical utility companies. This is due to the arrival of new non-SF₆ switchgear alternatives. Switchgear technology is now developing at a fast pace.

This dynamic, both technical and commercial, brings some uncertainty towards the adoption of non-SF₆ switchgear. Utilities in Norway and in France are now facing the dilemma of how to best navigate through this transition to non-SF₆ switchgear technology in the safest and optimum way.

This conversion needs to be achieved whilst maintaining the reliability of the equipment by following optimized maintenance procedures gained with 50 years of experience with SF₆ switchgears.

TSO have two main issues with SF₆ gas, the first is the GWP (Global Warming Potential) and the second (but related) is the repair and alarm aspect due to leakages or low temperature.

The pressure of the GIS equipment [1] has continuously increased since late 70's. A GIS bought in 1970 had a nominal filling pressure almost 70-90% lower than what TSO and DSO could purchase in 2020. Also, the new GIS product that are SF₆ free are expected to use a pressure that will be approximately doubled compared to what was provided in late 70's.

The reasons for this continuous increase are the competitiveness challenge of the GIS manufacturers to continually reduce the footprint and the cost of GIS equipment. Also, all alternative to SF₆, including C₄F_N mixtures need more pressure to reach the same level of dielectric withstand and switching capability. The combination of high pressure and higher dew point of C₄F_N gas mixture, lead end users to some liquefaction questions, that are not covered nor mentioned in any international standard.

Many pilot projects with alternative gases were done since the first announcement of available SF₆ free technology in Paris CIGRE Session of 2016. Following this, RTE has launched the energization of Grimaud 63 kV SF₆ free substation in 2018. Statnett in Norway have also implemented the first 420 kV 5000 A GIS with an outdoor temperature of -30°C using SF₆ free alternative, using C₄F_N molecules, for the passive parts, including busbar and outdoor busducts.

This paper presents one important aspect, the liquefaction characteristics, related to the challenges linked to SF₆ alternatives and the main related concerns and challenges facing the shift from well proven SF₆ switchgear to the new technologies.

2. INVOLVED PHYSICS

To evaluate the liquefaction properties of a mixture the knowledge of the phase diagram is essential. It represents the equilibrium between the different states of the substances as for example the vapour-liquid equilibrium (VLE). Contrary to single components where the VLE is represented by a line (called saturation line, dew line or bubble line), for mixtures, as the thermodynamics is more complex, the dew line and the bubble line are not identical, but they are enveloping the region of coexistence of vapour and liquid, see Figure 1. In the figure one can note the isochore line that represents the variations of pressure in function of the temperature at constant density. For example, if a closed compartment is filled at a certain pressure at 20°C and the temperature is decreasing the gas will follow the isochore line (decreasing of pressure at constant density) till the dew line where the first drops of liquid appear, and the gas starts to liquefy.

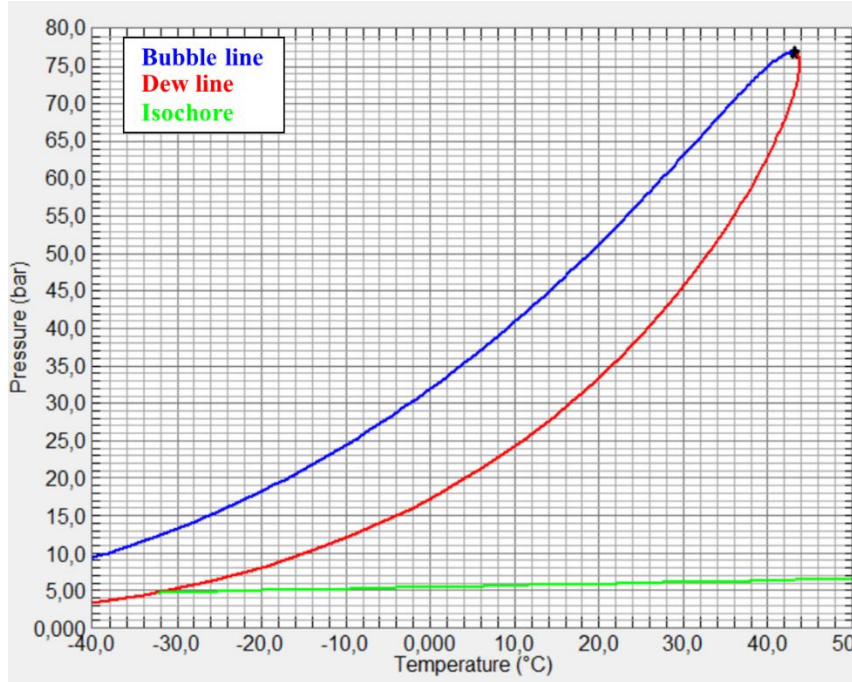


Figure 1 : Example of phase diagram for a C4FN mixture in CO₂ [2]

To describe the thermodynamics of substances, the equations of states can be used to relate the pressure, temperature, and volume (or density). The equation of state for real gases have been studied for centuries and the most known are the cubic equations of state of Van der Waals (1879), Redlich and Kwong (1949), Soave-Redlich-Kwong (Soave, 1972) and Peng-Robinson (1976). This models usually need the critical points, the molecular weight and the acentric factor of the substances. When coming to gas mixtures, the interaction between the molecules should be considered and models are more complex and requires interaction parameters that should be calibrated with experimental data. For example the equations of Peng-Robinson for mixtures that correlate the pressure (P), molar volume (\tilde{V}) and the temperature (T) can be written as in Eq.(1). The mixture parameters are described in Eq. (2)(3)(4) in function of the mole fraction of the different species (x_i) where k_{ij} is an adjustable parameter and the a and b coefficient for the different species can be written as in Eq.(5)(6).

PR equation	$P = \frac{RT}{\tilde{V}_{mix} - b_{mix}} - \frac{a_{mix}}{\tilde{V}_{mix}(\tilde{V}_{mix} + b_{mix}) + b_{mix}(\tilde{V}_{mix} - b_{mix})} \quad (1)$
	$a_{mix} = \sum_{i=1}^k \sum_{j=1}^k x_i x_j a_{ij} \quad (2)$
	$b_{mix} = \sum_{i=1}^k x_i b_i \quad (3)$
	$a_{ij} = (1 - k_{ij}) \sqrt{a_{ii} a_{jj}} \quad (4)$
Coefficient a_i	$a_i = 0.45724 \left(\frac{R^2 T_{ci}^2}{P_{ci}} \right) \alpha_i \quad (5)$
Coefficient b_i	$\alpha_i = [1 + (0.37464 + 1.54226\omega_i - 0.26992\omega_i^2) \cdot (1 - \sqrt{T_r})]^2$ $b_i = 0.07780 \left(\frac{R T_{ci}}{P_{ci}} \right) \quad (6)$

R is the universal gas constant, T_c , P_c and ω are respectively the critical temperature and pressure and the acentric factor and T_r is the reduced temperature

Regarding the thermodynamics of the equilibrium between the liquid and the vapour state (dew line) the equilibrium condition should be imposed in the model. This is usually done introducing the liquid and vapour fugacity coefficient [3]. The determination of the dew line thus needs iterative algorithm and can be complex due to convergence problems. Another approach is the description of the liquid vapour equilibrium by empiric equations that are determined experimentally. One of the most known is the Antoine equation, see Eq.(7), an empiric laws that permits the estimation of the dew point pressure in a certain range of temperature. The constants A, B, and C in the equations are determined in order to fit the experimental results.

Antoine equation

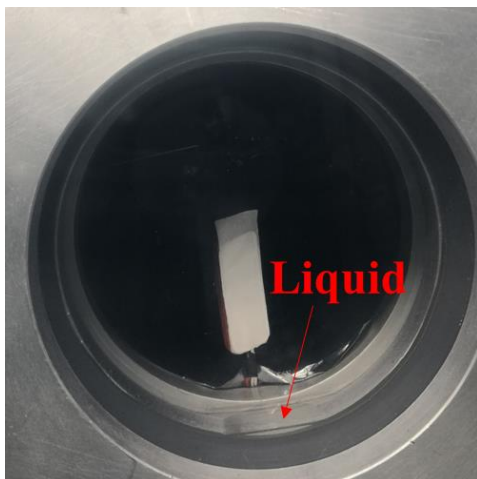
$$\log_{10} P = A - \frac{B}{C + T} \quad (7)$$

3. EXPERIMENTAL TEST

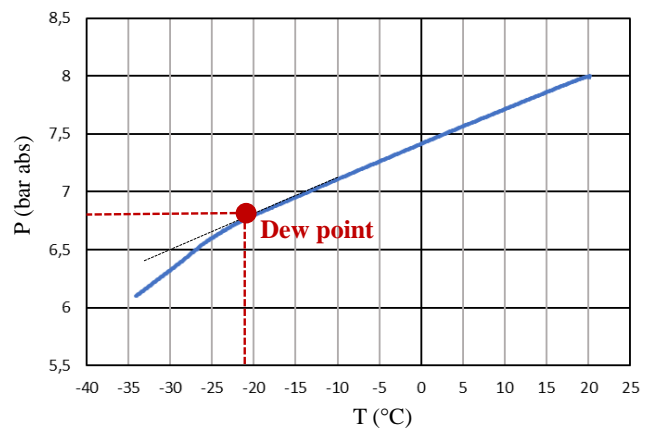
3.1 Methodology

Very low data are available in literature regarding the thermodynamic of the C4FN mixture with CO₂ and eventually O₂. To represent the thermodynamic of the mixtures and to assess the dew point of a certain mixture ratios the approach was to determine through experiments the interaction parameters for the three components (C4FN, CO₂ and O₂) in order to calibrate the theoretical Peng Robinson equations. These can then be used to correlate the pressure, temperature and the density of a certain mixture. Moreover, to determine the dew point curve, liquefaction tests are necessary for the evaluation of the coefficient of Antoine liquefaction equation.

The dew point for a specific concentration mixture with a certain density is determined by the intersection of the dew point curve and the isochore line (pressure variations due to the temperature changing at constant density). Thus, the dew point curve can be determined decreasing the temperature in a closed compartment filled with a certain pressure till the appearance of the first drop of liquid and then a liquid phase in the gas (Figure 2a). As it could be difficult to identify the first moment of apparition of the liquid, the liquefaction is determined by the drop of pressure. This drop is due to the density change caused by the presence of a liquid phase. An example of this slope changing can be seen in Figure 2b where the registered pressure is plotted in function of the temperature.



a)



b)

Figure 2 : a) Visual evidence of the presence of liquid in the gas phase. b) Isochore curve in the temperature/pressure plot till the slope changing due to liquefaction.

The liquefaction point, pressure at the liquefaction temperature, is determined using a numerical methodology which was validated by preliminary tests in SF₆, as detailed in section 3.3, and which was used identically each time to avoid human error contribution in data analysis. A linear correlation is

made on 700 measuring points close to the liquefaction point. When the difference between linear extrapolation and the measured curve is greater than 5%, the liquefaction point is established.

One should note that other methods exist for the determination of the dew point of mixture, as for example laboratory tests like the VLE tests where the dew pressure at dew temperature can be determined for different mole fraction of components in the mixtures. However, the approach used here has been chosen to be as close as possible to the real conditions that a HV equipment can experience when the external temperature drops.

3.2 Test set up and test protocol

The test set up is reported in Figure 3. It is composed by a 50 L pressurized metal enclosed compartment with a window for a visual, but only indicative, observation of the apparition of drops and a liquid phase. Two different measuring probes for the real-time acquisition through a Labview program are installed as shown in Figure 3. Indeed, for the scope of the test, the temperature and pressure of the gas should be monitored in order to identify the liquefaction point as explained in section 3.1. In order to do so two measuring devices are used:

- PT100 probe: for the measurement of the temperature thanks to a recorder;
- GDHT20 sensor: for the measurement of the temperature and pressure.

All the measuring equipment are calibrated by an external laboratory prior to test. The measurement uncertainty for the temperature and pressure measurement are respectively 0.3 °C and 0.02 bar.

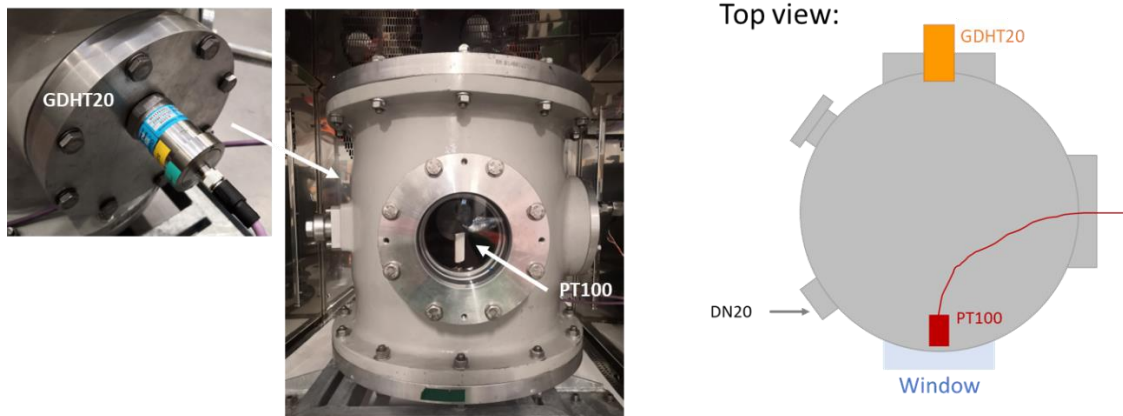


Figure 3 : Test set up with the position of the different sensors.

The test set up is installed in a climatic chamber that has a temperature range of -70°C/ +180°C.

It has been chosen, to study three different C4FN mixtures, reported in Table 1. The first mixture has been prepared with partial pressure methodology in a 950L vessels more than one month before the tests, while the two others has been purchased from a gas manufacturer in B50 bottles. As for the calibration of the equations it is really important to have the correct mole ratio of the components in the mixture, IRTF/GCMS laboratory analysis has been done or requested for each mixture. The results are as well reported in Table 1.

Table 1 : Investigated mixtures.

Mixture	Laboratory analysis results	Uncertainty
6% C4-FN – 94% CO ₂	5,5% _{mol}	±0,2% _{mol}
6% C4-FN – 5% O ₂ – 89% CO ₂	5,85% _{mol} C4FN + 5,03% _{mol} O ₂	±3% _{mol} rel
3,5% C4-FN – 13% O ₂ – 83,5% CO ₂	3,40% _{mol} C4FN + 13,10% _{mol} O ₂	±3% _{mol} rel

Differential pressure filling method has been used to pressurize the test compartment.

For each mixture six pressures have been studied, starting from 5 bar abs and increasing the test pressure of one bar after each test till 10 bar abs. The cooling cycles has been settled as shown in Figure 4, it has been defined after preliminary tests. Two hours at 20°C are kept in order to register the pressure at the reference temperature of 20°C, after the temperature is cooled down till -40°C with a slope of 0.4 K/min. The temperature of -40°C is kept for 2 hours/3 hours and then fixed back to 20°C with the same slope of the cooling part. The lower temperature has been fixed to -40°C due to limitation of the measuring probes. The temperature of 20°C is then kept for 6 hours to restabilize the temperature in all the gas volume.

For each cycle the data collection from all the sensors is done every three seconds.

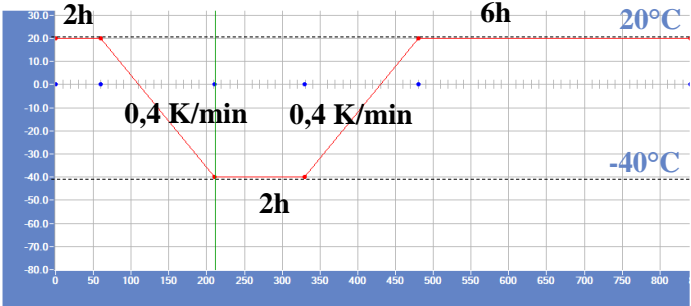


Figure 4 : Applied cooling cycle

3.3 Preliminary test

To validate the test protocol and to identify the best positions for the PT100 temperature probe, preliminary tests were conducted in SF₆. As the liquefaction point of SF₆ is well known, those preliminary tests have the scope to also validate the methodology used for the analysis of the results. The test is conducted at 7.94 bar abs of SF₆ at 20°C. The expected liquefaction temperature at the tested density, calculated with REFPROP [2], is -21.94°C.

First three different cooling cycles are applied in three different days to validate the test protocol and the repeatability of the measurements. The relative isochoric cycles are displayed in Figure 5 coming from the measurement of the pressure/temperature registered by the GDHT20 sensor. One can note a very good agreement between the different tests confirming the repeatability of the measurement. One can note also that the values are close to the expected dew point temperatures.

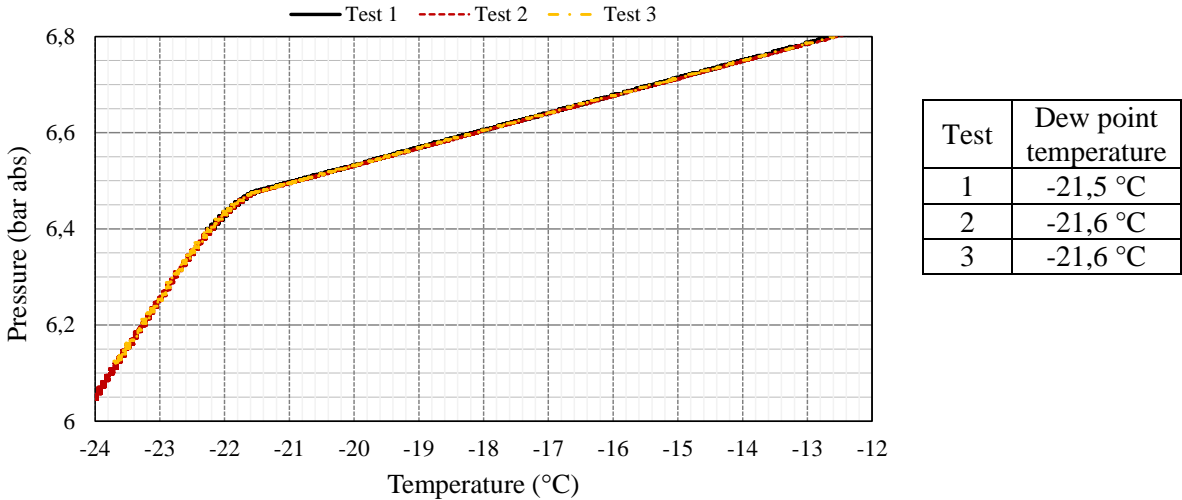


Figure 5 : Three isochoric scans for SF₆ at 7,94 bar abs at 20°C and the dew point temperature of each's.

Three probes are then installed at three different positions inside the test compartment, as shown in Figure 6. The dew point measured by those three different temperature probes are reported in

Table 2. For the determination of the dew point through the methodology explained in section 3.1 the pressure is the one measured by the GDHT20 sensor. One can note that the found values are not so different between each other's and in accordance with the values measured by the GDHT20 sensor (max difference 0,5 °C). Afterwards, for the following tests it has been chosen to keep only one temperature probe the one in the position T1.

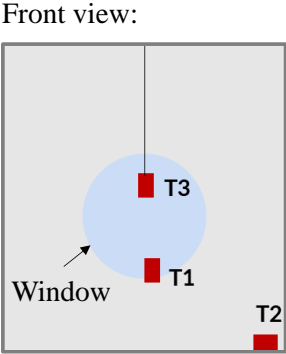


Table 2 : Dew point temperatures determined through the different measuring systems.

Sensor	Dew point temperature
T1	-22,1 °C
T2	-22,0 °C
T3	-21,8 °C
GDHT20	-21,6 °C

Figure 6 : Positions of the three different temperature probes.

3.4 Results

An example of the isochoric curve of the measured pressure by the GDHT20 sensor and the measured temperature of the same sensor and the PT100 is reported in Figure 7 for the 5.5% C4FN mixture at 8 bar abs at 20°C. The corresponding dew points are also displayed in figure. As the results of the two sensors are very similar for the following representations and for the analysis only the dew point coming from the GDHT20 sensor are employed.

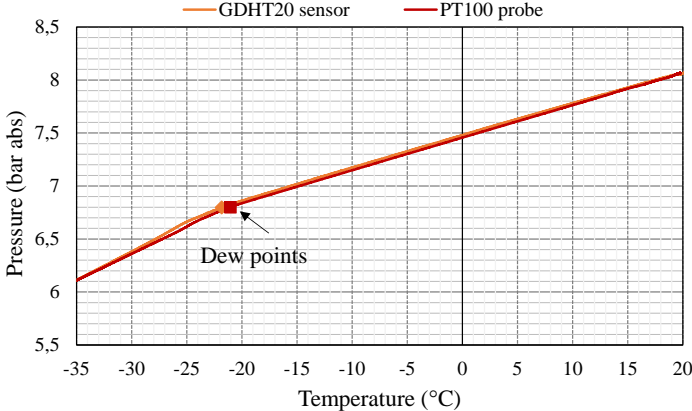


Figure 7 : Isochoric scan till the liquefaction for the 5% C4FN mixture at 8 bar abs at 20°C measured by the two measuring systems.

As detailed in section 3.2 three mixtures have been tested. The dew points of those mixtures are displayed in Figure 8. One can note that the liquefaction points of the mixtures 5,5% C4FN and 5,85% C4FN/ 5,03% O₂ are close. As observed in literature the increase of O₂ content could increase the liquefaction temperature [4]. This is coherent with the observed results as even if the 5,85% C4FN/ 5,03% O₂ mixture has a little higher C4FN content the liquefaction is almost at the same values than the mixture 5,5% C4FN.

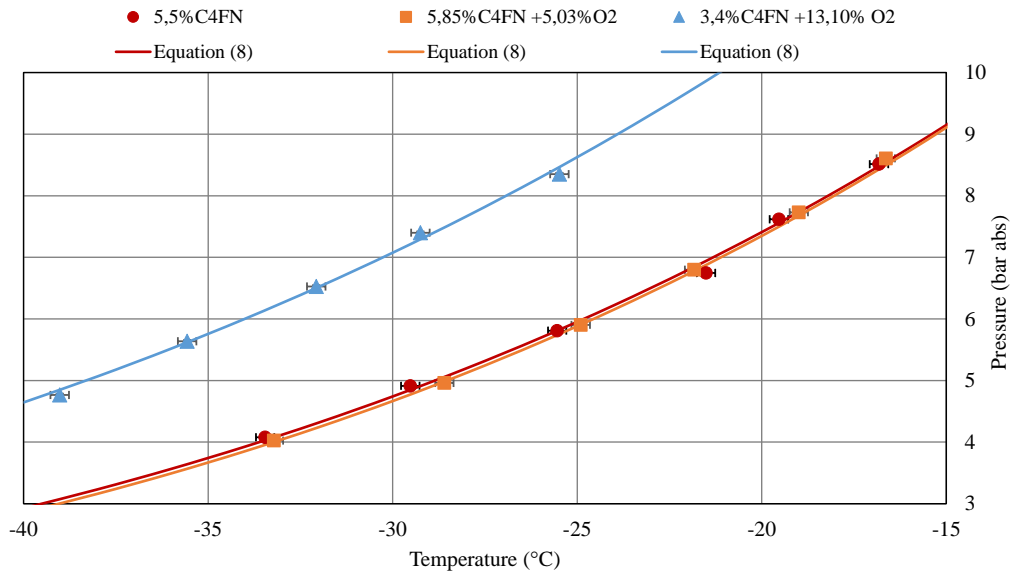


Figure 8 : Dew lines for the three tested mixtures as per Eq.(8) and the experimental dew points.

The experimental data have been used for the determination of a fit equation, with the form of the Antoine equation in (7) but that includes the dependencies of the concentration of C4FN (x_n) and O₂ (x_o) in the mixture. This equation can be expressed as follow:

$$\log(P) = (A_0 + A_1 * x_n) - \frac{(B_0 + B_1 * x_n + B_2 * (x_n)^2 + B_3 * x_o + B_4 * x_o^2)}{C + T/^\circ C} \quad (8)$$

For the three mixture the calculated dew line through this equation is reported in Figure 8. One can note that the maximum error in the fit is 0.7°C. One should note that the validity of this equations should be considered within the tested mixtures, i.e. C4FN content between 3% and 6%mol and O₂ content till 13%.

A comparison between the equation Eq. (8) and dew point equations proposed in literature in [5] and in [6] are displayed in Figure 9 for the two tested mixtures (5,85% C4FN + 5,03% O₂ and 3,40% C4FN + 13,10% O₂). Depending on the mixtures the difference at equal dew point pressure can reach 2°C, this is probably due to different ranges of validity and uncertainty in the experimental tests.

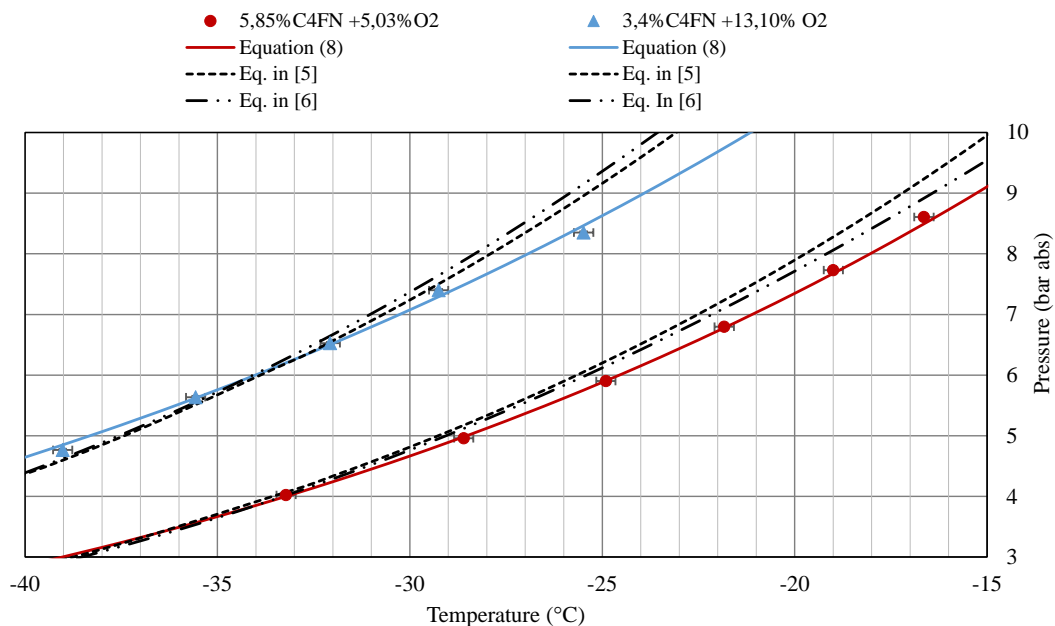


Figure 9 : Comparison between dew line from Eq. (8) and from [5] and [6].

4. CALCULATION TOOL AND PRACTICAL APPLICATIONS

The interest of the experimental tests was to increase the knowledge on the thermodynamic behaviour of C4FN mixtures and being able to determine the dew point of C4FN mixtures at different molar contents and densities. In normal operating conditions the equipment filled C4FN mixture are normally certified not to liquefy even if partial liquefaction at particular conditions might be acceptable [6]. However lower temperatures may occur or concentration changing due to differential permeation or refilling during the lifetime of the equipment. For users it is very interesting to being able to evaluate the need or not to intervene to maintain good characteristics of insulation for switchgears.

From a practical point of view, the OEM communicate information to the users to have the thermodynamics characteristics at the nominal rate of the mixture. However, during the lifetime of the GIS, the gas filled from the commissioning will change due of switchgear leakage (i.e. for GIS, leakage rate for routine test is 0.5%/year in IEC 62271-203: 2022). The evolution of the mixture during lifetime and all the characteristics of the new gas implemented and used is one of important information who users need to know to make their own asset and risk management for equipment lifetime.

Due to the consistent number of data acquired during the test campaign, either dew points or isochoric scans, the experimental measurements have been used to obtain equations that allows, within a certain validity range, the description of the thermodynamic behaviour of mixtures with different molar ratios of C4FN, O₂ and CO₂ and at different densities. To represent the state equations for the fluoronitrile mixtures, the Peng-Robinson equation, described in Eq.(1) has been used. With the collected data the correlation parameters between the different components of the mixtures have been determined. This equation permits the determination of the variations of pressure due to the temperature changing and to reconvert at the reference temperature, usually 20°C, the measured pressure.

For the evaluation of the liquefaction point for a specific C4FN mixture concentration a software has been developed in Python 3. The implemented equations are the Peng Robinson EOS calibrated with the experimental data and the liquefaction curve fit equation in Eq.(8), see Figure 10.

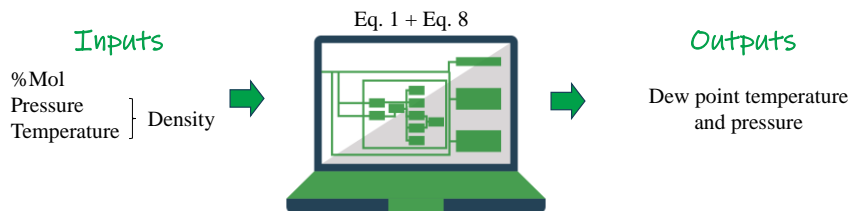


Figure 10 : Schematic view of the implemented software.

An overview of the software is shown in Figure 11.

This software responds to the need of TSO to a fast and onsite check of the thermodynamic properties of the exploited mixture in their switchgear assets even if the mixtures has been changed from the nominal initial rate.

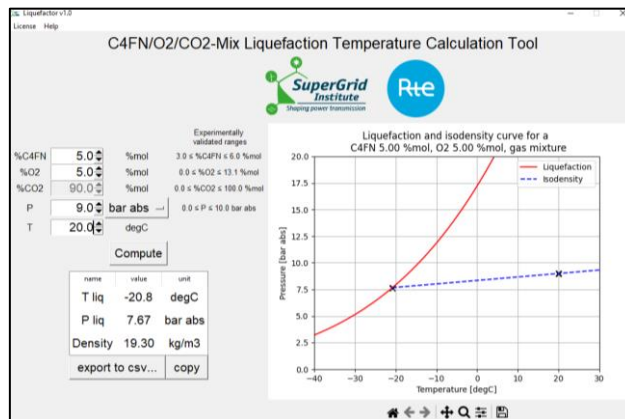


Figure 11 : Overview of the implemented software.

5. CONCLUSIONS

Following the need to increase the knowledge of TSOs on the liquefaction properties of fluoronitrile mixtures, experimentation has been conducted to increase the thermodynamic knowledge on these types of mixtures and to determine equations to represent the isochore and liquefaction curves. Three mixtures, with different C₄FN content with and without O₂, has been characterized with a thermodynamic experimental approach. Isochoric scans till dew points have been done in a pressurized GIS vessel in a climatic chamber. The used approach was meant to be as close as possible to the real conditions that a HV equipment can experience when the external temperature drops.

The consistent number of data acquired permitted the definition of equations that allows, within a certain validity range, the description of the thermodynamic behaviour of mixtures with different molar ratios of C₄FN, O₂ and CO₂ and at different densities.

To respond to users' need of fast and onsite check of the mixture properties, a software that includes the obtained thermodynamic equations has been developed.

The experimental approach used for the investigations and the developed software were made for users who want to increase their knowledge about C₄FN mixtures used as SF₆ alternatives.

The developed software is meant to answer to the TSO need to deal with the new challenges linked to the use of C₄FN mixtures in their assets.

This new tool is part of modern instruments for all users who are dealing with C₄FN mixture as alternative to SF₆.

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