

Freezing curve development for road and airport deicers: phase transition temperature determination by Raman spectroscopy

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ABSTRACT

Winter maintenance is based on interventions of operating services, as well as on the use of de-icing products. In France, the common practice is to apply sodium chloride on the French road network, and the runway de-icing fluids (mainly sodium or potassium acetates and formates) on the aeronautical surfaces. Dissolved in water, these products lower the solution's freezing point, promoting the melting of an ice film at negative temperatures. The knowledge of phase diagrams is thus necessary for the determination of quantities to apply and represents a lever for the optimization of de-icing operations according to given road weather conditions.

The Center of Technical Studies of the East (CETE de l'Est) developed a spectroscopic method for the determination of phase transition temperatures for aqueous solutions and the identification of their phase diagrams. This paper describes the application of this method on RDF products and presents a comparison between their experimental phase diagrams.

1. INTRODUCTION

Winter maintenance is based on the intervention of operating services. These interventions are mainly based on the spreading of anti-icing or de-icing chemicals on pavements in order to ensure secure conditions for the traffic. The role of these chemicals is to prevent the formation of ice and to provoke its melting [1, 2] in order to maintain a proper grip level for road traffic. This is obtained thanks to their capacity of reducing the freezing point of the water/ice mixture present on a pavement [3, 4].

The type of de-icing and anti-icing chemicals used depends on the surfaces that need to be treated, but also on country policies. In France, the common practice is to apply sodium chloride on the road network. On aeronautical surfaces, the usage of chlorides is prohibited due to their highly corrosive property, which make them possibly dangerous for airplanes [5]. The products used in these conditions, the runway de-icing fluids (RDF), are of different nature and are mainly based on sodium or potassium acetates and formates. Furthermore, these products contain also corrosion inhibitors which permit the reduction of the airplane risks [6, 7].

Several parameters define the efficiency of the products, the main ones being their active compound, as well as their concentration. The more efficient the product, the lower its freezing point. In order to evaluate precisely whether a de-icing treatment is required according to encountered weather conditions, it is necessary to know the RDF's phase diagram. Even though the phase diagrams of pure sodium or potassium acetates and formates are known, it is not true for commercial products that are actually applied. Indeed, in these commercial products some corrosion inhibitors are added in order to

diminish the airplane corrosion risks. However, these additives may influence the solution's freezing point, making the RDF phase diagrams unknown.

In this paper, we shall show that Raman spectroscopy can be used for the RDF characterization with the objective to optimize the quantities that are applied. In that purpose, several methods based on Raman spectroscopy were developed for the characterization of aqueous solutions [8-11]. The results of the application of these methods on RDF products will be presented here. A comparison between phase diagrams of different products will be presented, showing the differences in their efficiency.

2. PRODUCTS ANALYSED

The analysis was performed on materials used as RDF aFrostnd supplied by industrials. In collaboration with the French Technical Service of Civil Aviation (STAC), several studies on RDF characterisation are led. These include liquid RDF products, 3 for each active compound (potassium acetate and potassium formate), and solid RDF products, 2 per active compound (sodium acetate and sodium formate). In this paper, results obtained on four commercial products (one per active compound) will be presented.

Dilutions of each product were prepared and analyzed as a function of temperature in order to determine its freezing point. For the spectra acquisition at low temperatures, a THMSG Linkam thermal stage coupled to a BWTek iRaman spectrometer was used. This stage gives access to a temperature range from -197 to 600°C, with $\pm 0.1^\circ\text{C}$ accuracy. The whole experimental setup is illustrated in Figure 1.

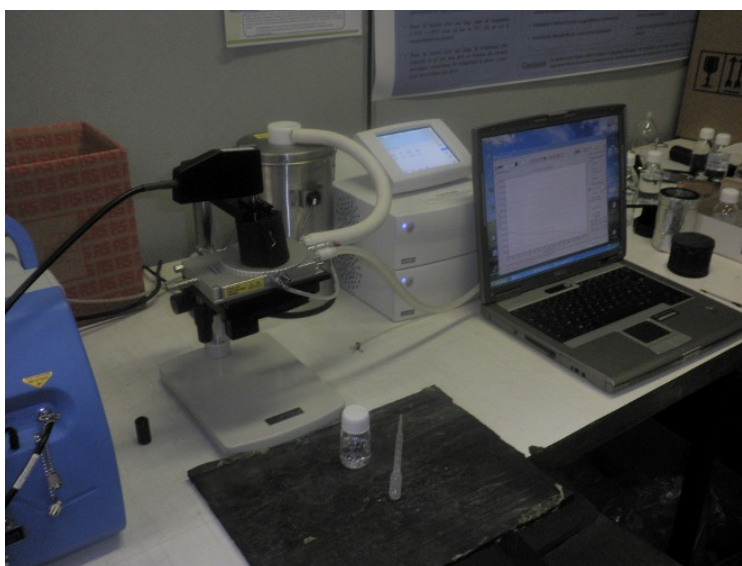


Figure 1. Experimental setup for the phase transition determination by Raman spectroscopy.

3. EXPERIMENTAL

3.1. Raman spectroscopy

The principle of the spectroscopic tool is to study the vibrations taking place within a material submitted to a laser beam. These vibrations are characteristic of the material structure and are probed by the energy difference between the incident exciting light beam and the light diffused on the sample. This energy difference depends on the type of molecule vibrations taking place.

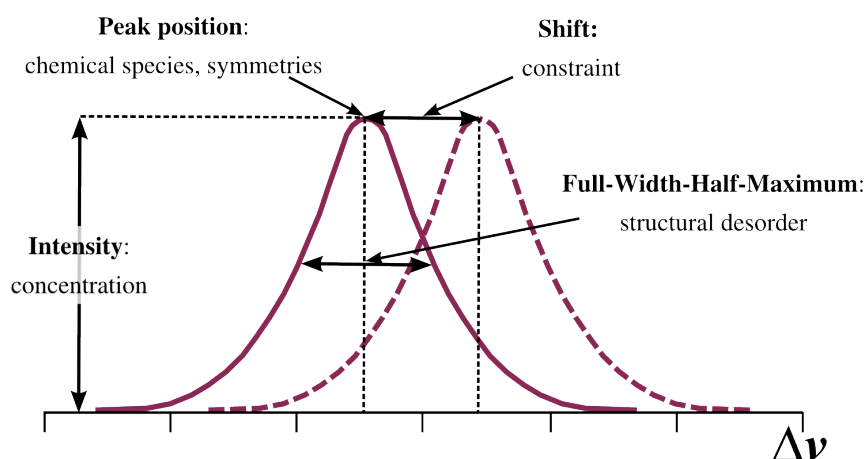


Figure 2. Information that can be deduced from a Raman peak [12].

A Raman line is specific of a chemical bond, the exploitation of the Raman peaks can therefore give us information on the material's structure, or the chemical concentration (Figure 2). A Raman spectrum carry information on the sample nature (structure, chemical composition), cristallinity, order degree ...

3.2. Spectroscopic phase signatures and temperature impact

Since Raman spectroscopy permits to probe the sample's structure, it can be used to determine a solution's phase. Indeed, as the sample's phase change, there are several changes in the sample's characteristic peaks: a wavenumber shift is observed, along with the relative intensity change [13]. This can be viewed in Figure 3 where Raman spectra of water and ice are presented.

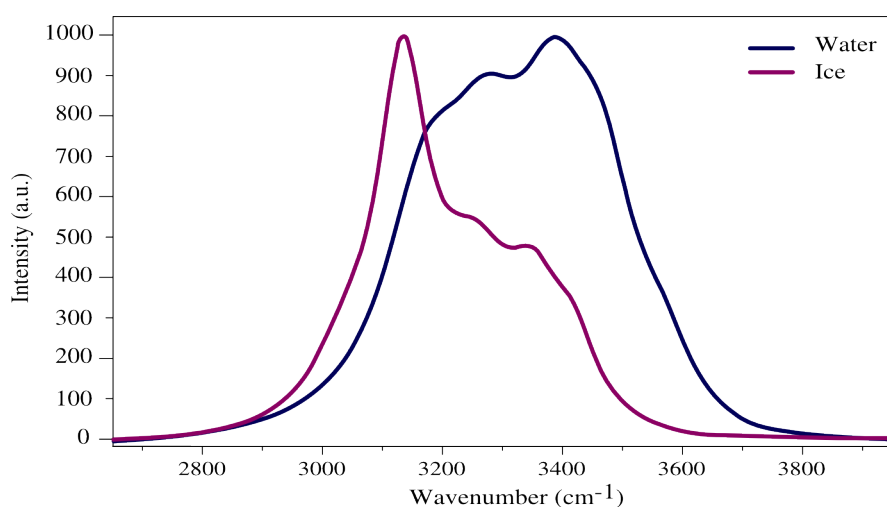


Figure 3. Influence of a sample's phase on its Raman spectrum: comparison between water (up) and ice (down)

The information on the solution's phase can therefore be obtained by acquiring only one Raman spectrum of the RDF sample, as the simple presence of the peak located at 3120 cm^{-1} indicates that the sample is in its solid phase. This characteristic has been used for the definition of a spectral marker S_D , which can permit the extraction of the phase directly from a Raman spectrum.

To determine the sample's phase transition temperature, it is necessary to follow-up of the changes occurring during a temperature change. The analysis of the aqueous solutions by Raman spectroscopy permitted to identify the evolution of their spectral signatures as a function of the solution's temperature. The temperature impact on a Raman spectra of a solution of potassium formate can be observed in Figure 4.

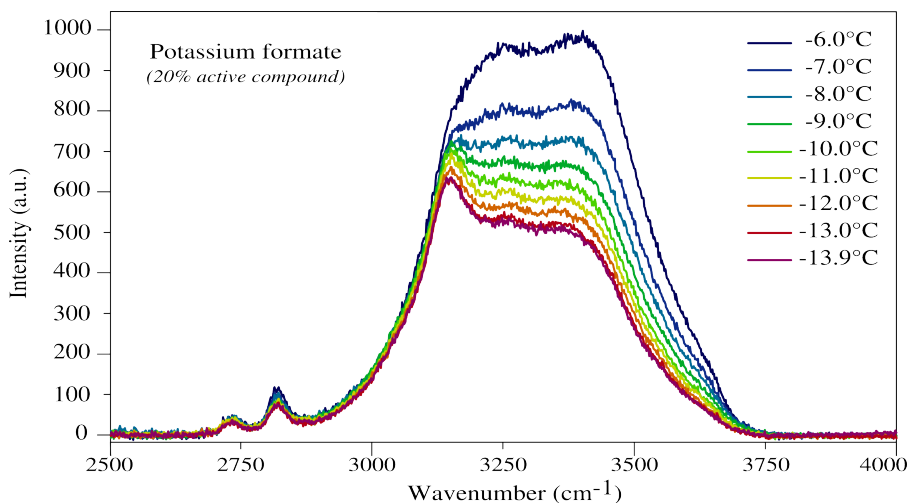


Figure 4. Temperature influence on the sample's Raman spectrum around its phase transition

A spectral marker which could be correlated to the solution's phase transition was defined. This marker is related to the evolution of the integrated intensities of ice and water characteristic peaks [10].

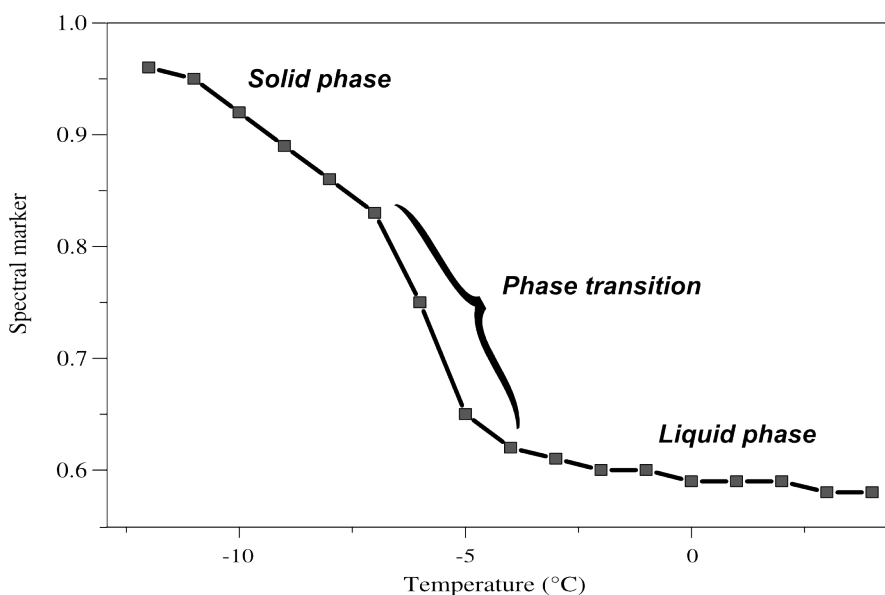


Figure 5. Temperature influence on the spectral marker evolution obtained for a 20 g/L solution of potassium formate.

The experimental curve based on the temperature influence on the spectral marker evolution is presented in Figure 5. This is an example of curve used for the phase transition determination.

3.3. Phase diagram construction

The analysis of one product's solutions at different concentrations and the determination of their freezing points permit to construct that sample's phase diagram. Five dilutions of each RDF analyzed were prepared and their freezing points determined. The obtained phase diagrams are presented in Figure 6.

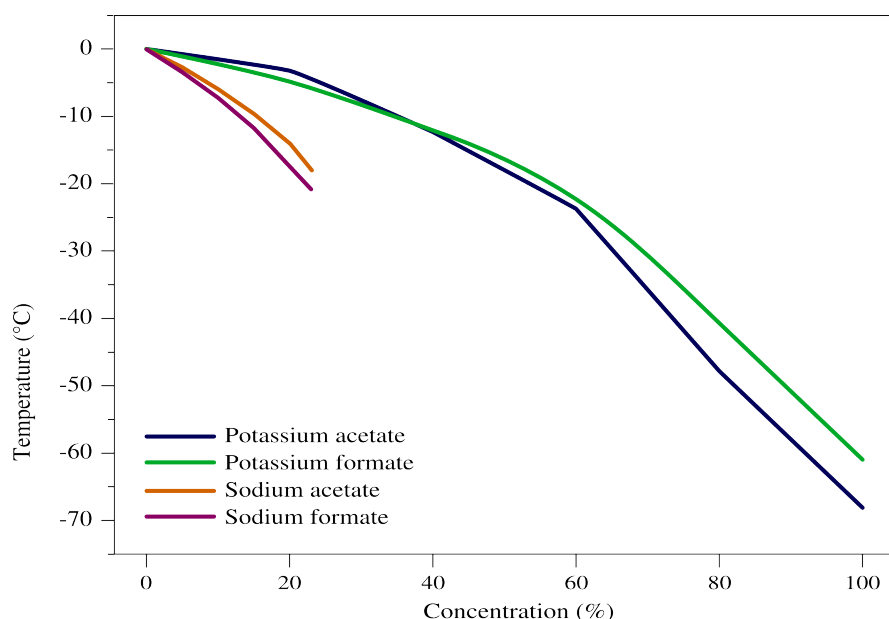


Figure 6. Examples of phase diagrams of solutions of liquid RDFs (potassium acetate and potassium formate) and of solutions of solid RDFs (sodium formate and sodium acetate)

As expected, the decrease of the freezing point with concentration increase can be observed. It is to note that the weight percents correspond to the percentage of commercial products in the solution. Hence, the potassium acetate and formate being commercialized in the liquid form, a 100% solution corresponds to a solution containing around 50% of the active compound. The commercial products based on sodium acetates and formates are in their solid form, and a pure commercial product can contain over 95% of the active compound.

The biggest difference can be observed between the liquid and the solid RDF phase diagrams. This difference can be explained by the fact that the pure liquid RDF contain twice less of the active compound than the pure solid RDF, making it much less efficient at same concentration of commercial product. Furthermore, a slight difference can be observed between liquid RDF, as well as between solid RDF. This could indicate the influence of the anion (acetate or formate) used as the RDF active compound. Since for the liquid RDF it is the acetate that seems to be more efficient, and for the solid RDF, on the contrary, the formate, the corrosion inhibitors might have an influence on the solution's freezing point.

4. CONCLUSIONS

Spectra of sodium and potassium acetate and formate aqueous solutions at different concentrations and at temperatures below 0°C were recorded and analyzed by Raman spectroscopy in order to build their phase transition diagrams.

A method for the phase transition determination was developed. This method is based on the analysis of the evolution of the ice and water characteristic peaks. A phase marker S_D was defined and used for the construction of phase diagrams.

Phase diagrams indicated a decrease in the solution freezing point as the salt concentration increases. The freezing point at maximum concentration is the principal criteria for deicer's performance. The knowledge of the RDF phase diagram can permit the optimization of the quantities that need to be applied.

The development of Raman spectroscopy in the last decades permits the possibility of deploying a spectrometer directly on airport airways for *in situ* measurements, which is one of the perspectives of this work. Indeed, the CÉTÉ de l'Est is now developing a sensor based on this technique for the *in situ* determination of the phase and the residual amount of these products on airport runways.

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