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RHEOLOGICAL STUDY OF TWO-PHASE SECONDARY FLUIDS FOR REFRIGERATION AND AIR CONDITIONING.

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Abstract. The two phase fluids have promising application in refrigeration thanks to their large cooling capacity and their storage ability. However, the lack of information on their properties makes the selection of a proper fluid uneasy. An experimental set-up inspired from the scrapped surface heat exchanger technology is presented in this paper. It was developed both to generate and to characterise slurries in a rheological point of view. The large range of temperature envisaged here allows enlarging the field of application of the technology to cooler temperatures (freezer applications) and to positive ones (air conditioning systems). The principle of the viscosity measurements is described on solutions of ethyl alcohol; a hydrate is also presented as an example of compound showing a dissociation temperature in the range concerned by air conditioning applications.

INTRODUCTION

Because it is nowadays necessary to phase out CFCs or HCFCs fluids from the refrigeration industry, indirect refrigeration systems renews interest as they enable to notably reduce the use of environmental non-friendly fluids. In particular, the ice slurries were carefully envisaged as secondary refrigerants because of their great heat capacity (up to 10 times higher than conventional mono-phase refrigerants), which could allow to reduce in a ratio 1:3 the dimensions of the plants [1]. Moreover, such a technology ensures the transport of a constant low temperature fluid, and offers an energy storage capacity which is really interesting in an economical point of view (the ice is generated during the cheapest electricity periods). All the advantages are linked to the solid / liquid nature of the ice slurry, so that any other crystallised solid compound could *a-priori* be envisaged, provided that it has a sufficient heat capacity, an adequate melting point temperature and a low viscosity. In particular, two-phase fluids with a positive freezing point enlarge the applications fields of the technology from the refrigeration applications to the air-conditioning systems.

However, this kind of process only remains interesting if the solid fraction of the slurry is sufficient, and the viscosity of the suspension is not too important. The technology turned to give good results with slurry at $\square 5^{\circ}\text{C}$ (refrigeration units already exist, mainly used for display cabinets cooling in supermarket). It is now a real challenge to develop the process for freezer application [2], where most usual refrigerant fluids give really viscous slurries at $\square 35^{\circ}\text{C}$. In the same way, it is still open to find an appropriate candidate for an air conditioning application. Gas hydrates are promising materials because of their positive freezing temperature, they are widely used in Japan (mainly as phase change materials for thermal energy storage), but the ones currently employed will be confronted to environmental restrictions in the very next years.

The lack of information on the two-phase refrigerants properties makes the selection of a proper fluid uneasy. The experimental set-up presented in this paper was developed to characterise the viscosity of slurries. It has been built up in the context of an European project

(acronym ICECOOL [3]) which aims to develop a new machines to produce $\approx 35^{\circ}\text{C}$ ice-slurry. Precise specifications were defined concerning the fraction of ice and the viscosity we want at this temperature; we will see on ethyl alcohol solutions how it is experimentally measured. A hydrate, which was given to be a potential candidate for an air-conditioning application [4], is also presented as an example of salt solution showing a positive melting point temperature.

EXPERIMENTAL SET-UP

The principle of the set-up is the one of an indirect refrigeration system, where a primary refrigerant is cooling a secondary one (the future slurry). The way the slurry is generated is inspired from the scrapped surface heat exchanger technology and a circulation loop has been instrumented to characterise the fluid viscosity. A schematic view of the set-up is given in Figure 1.

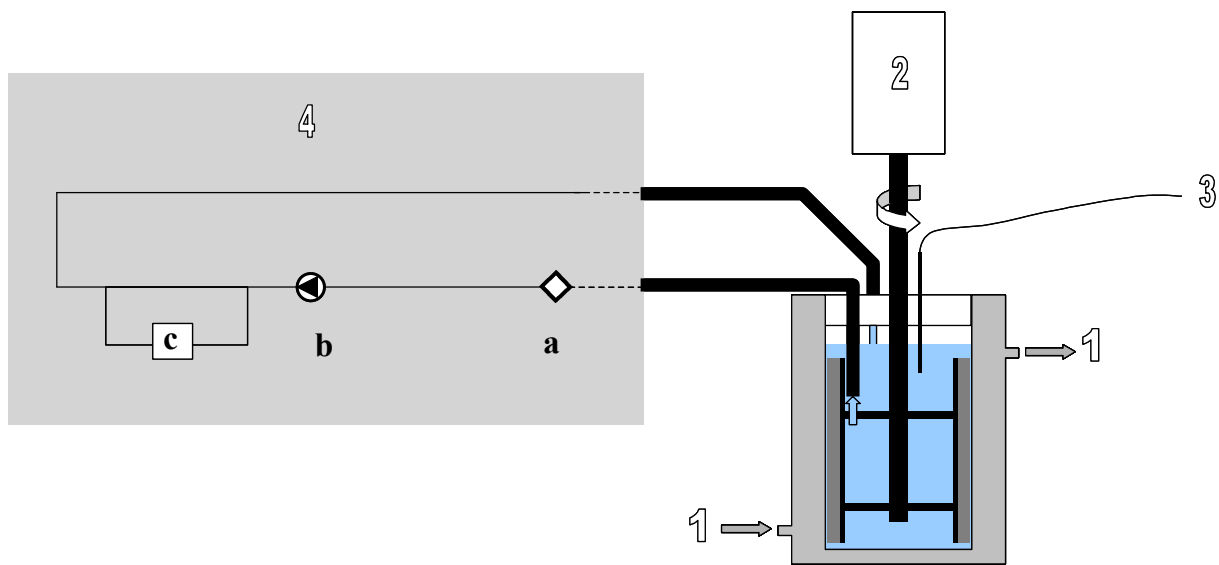


Figure 1: Schematic representation of the experimental set-up.
 (1): Primary refrigerant circulation; (2): Stirring and scraping system; (3): Temperature sensor; (4): Circulation loop (a: flowmeter; b: slurry pump; c: differential pressure transducer)

1. Slurry generation

A cryogenic fluid ((1) in Figure 1), cooled by a refrigeration unit, is circulating in the cooling jacket of a batch steel reactor (internal diameter: 150 mm; high: 250mm). It gradually cools the temperature of the fluid to be tested, previously poured in this crystalliser. In order to avoid an ice crystallisation at the reactor wall, a self-made agitation system (Figure 1 (2)) continuously turns and brushes the reactor surface.

2. Slurry characterisation

The experimental characterisation on the tested fluid is mainly a temperature measurement and a viscosity calculation.

The temperature is measured by a platinum temperature sensor (Pt100; accuracy: ± 0.1 C) set within the fluid itself, not too close to the reactor wall where the temperature tends to be a bit lower. Two other measurements are done in the flow loop pipe.

The rheological properties are determined by the measurements of a *pressure drop* and a *flowrate* in the external pipe. The fluid circulates in a loop of around 5 m long. Before the

measurement of the pressure drop, the fluid velocity pattern is first stabilised on a 0.5 m straight section (see Figure 2) to reach an established regime. Then the pressure drop is measured on a 1 m long, $\frac{3}{4}$ inch diameter straight pipe (internal diameter 1.575 cm). It has been instrumented with a 0-200 mbar differential pressure transducer (accuracy: ± 0.1 mbar). The flowrate is measured with a liquid industrial flowmeter (flow range: 0.2 - 40 l/min; accuracy: ± 0.5 %).

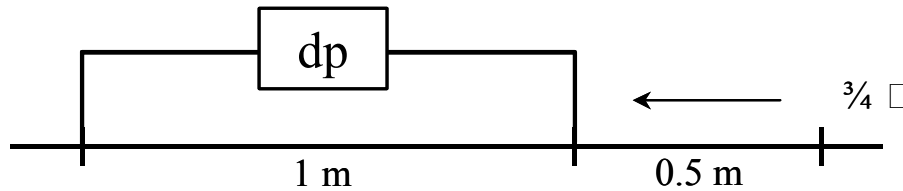


Figure 2: Measurement section

The whole system needs around 4.5 l of fluid to perform an experiment. Moreover, all the installation had to be strongly insulated (lid on the reactor, thick insulation moss) to minimise the heat losses (in order to work with fluids with low freezing point temperatures).

FLUID CHARACTERISTICS

This paper presents experiments performed both on ice and hydrate slurries. Ice slurries are obtained from ethyl alcohol solutions, which are well known for refrigeration applications. The hydrate slurry is obtained with an aqueous solution of an alkylammonium salt (tetra-n-butylammonium bromide (TBAB)). It has been patterned by Takao *et al.* as a candidate for air conditioning applications.

For our application, the phase diagram is an essential information that gives the thermodynamic conditions required to form a two phase fluids. For the envisaged solutions, they are available in the literature. Figure 3 gives the well known freezing diagram of ethyl alcohol in the mass range concerned by our experiments. It also remembers how the ice fraction can be deduced from such a diagram.

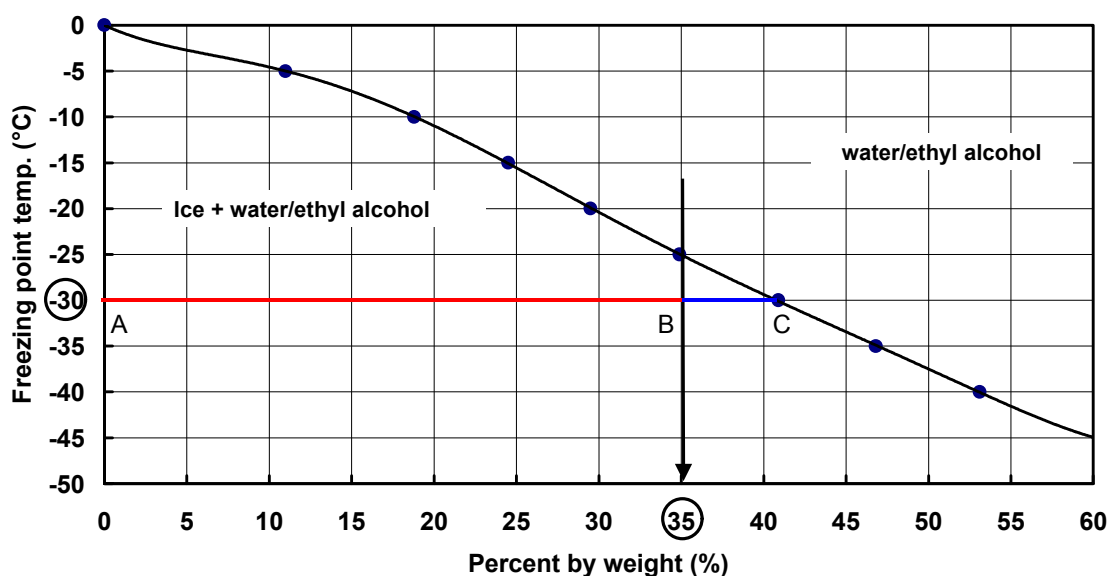


Figure 3: Freezing point diagram of an ethyl alcohol/water mixture (values from [5]). The ice fraction w at a given temperature (-30°C in this example), for an initial concentration of ethyl alcohol (35 % here) is given by $w=BC/AC$

For an unknown fluid, the same kind of diagram can be deduced from the cooling kinetic of the solution. This method has been applied to experimentally measure the phase diagram of the TBAB. The Figure 4 shows how it was determined: the first step consists in making the hydrate slurry in a two liters double-jacketed reactor; the second step is the dissociation of this hydrate. So, the temperature of the cryogenic fluid circulating in the cooling jacket is first progressively decreased and induces a cooling of the solution. In Figure 4, the nucleation is detected by a sudden temperature increase, up to the equilibrium temperature. In the TBAB particular case, it can be seen that this compound presents a high supercooling, in the order of 10°C . Then, the temperature of the cooling jacket is progressively increased. The sudden change of dT/dt marks the end of the dissociation (and thus gives the dissociation temperature).

In Figure 5, the difference observed between our experimental diagram and the one obtained by Takao et al. (with a differential scanning calorimeter) must be due to a kinetic of heating higher than the dissociation kinetic of hydrates (we imposed quite a rapid heating kinetic, of the order $1^{\circ}\text{C}/\text{min}$). Measurements with slower heating should certainly lead to closer curves.

Anyway, this diagram indicates that hydrate compounds are likely to be employed in air conditioning system as they can offer a dissociation temperature in a range appropriated to this application.

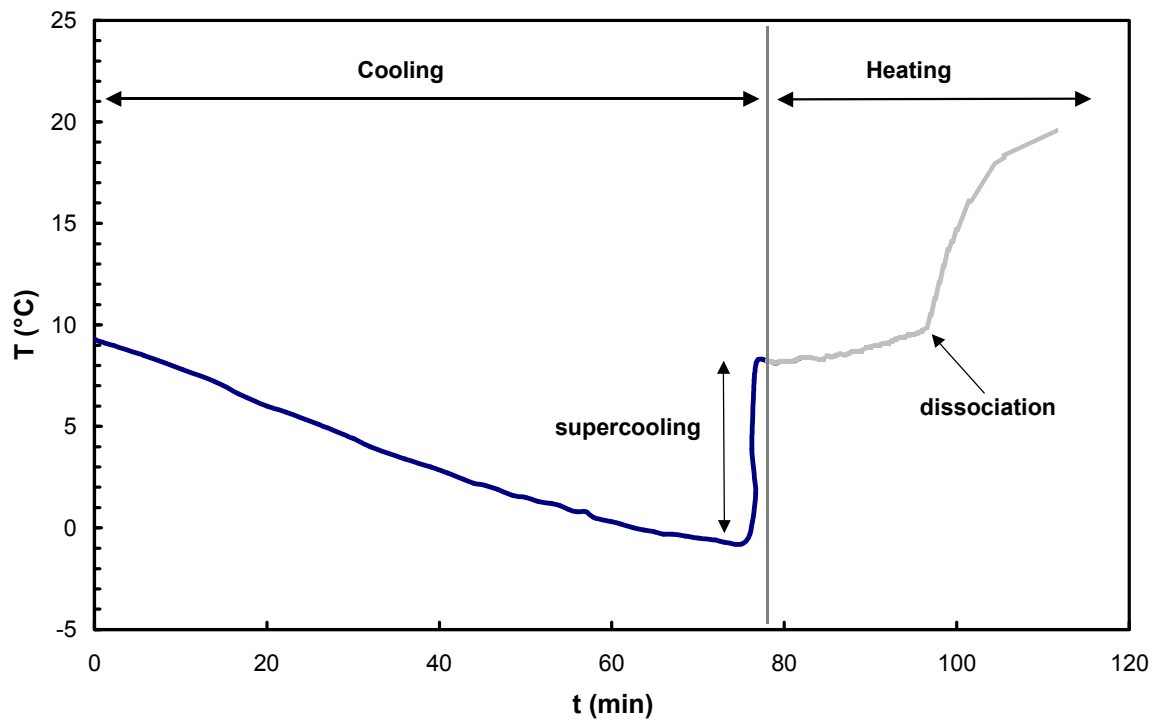


Figure 4: Cooling and dissociation kinetics of 1.5 liters of a 20% of TBAB solution. A high supercooling is observed.

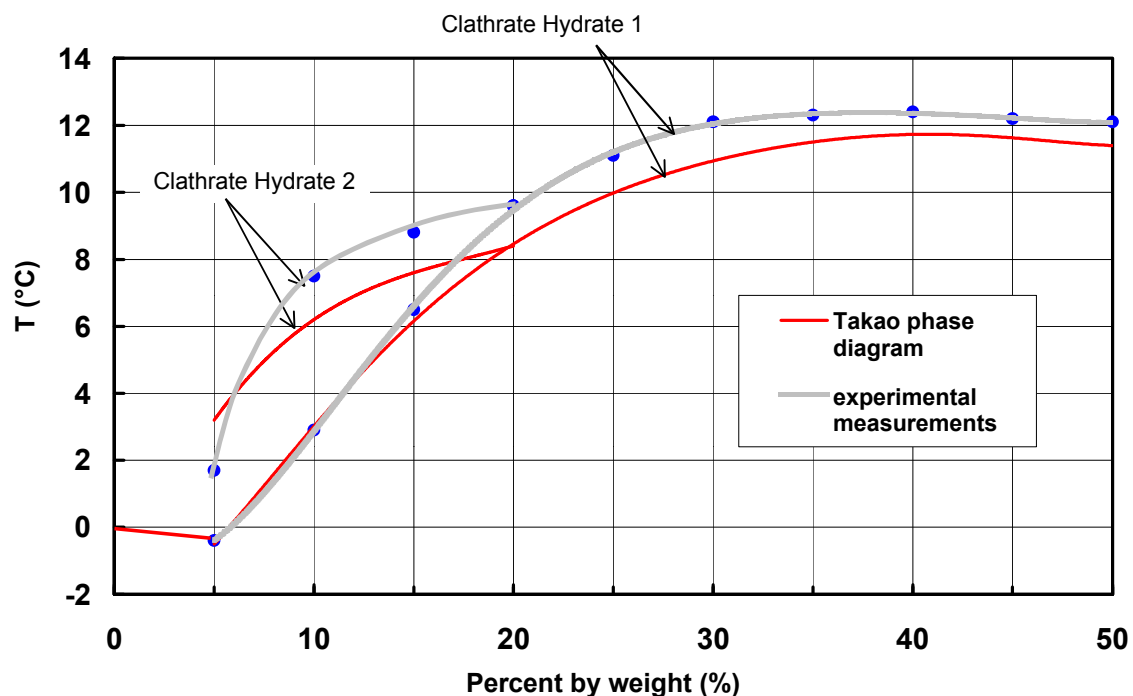


Figure 5: Phase diagram of TBAB. Comparison between the diagram of Takao [4,6] and the experimental data obtained by the thermal analysis of the hydrate dissociation. Two hydrates can form (the clathrate hydrates 1 and 2 are differentiated by their hydration number [4]).

EXAMPLE OF MEASUREMENTS

The Figure 6 presents experiments performed with solutions of three different concentrations of ethyl alcohol and two different concentrations of TBAB. The measured pressure drops strongly increase when the first ice or hydrate crystal appears. It is to mention that, contrary to hydrate formation, we do not observe any induction period or supercooling before the ice formation. In fact, by comparing Figure 6 to Figure 3 and Figure 5, one can see that the freezing points obtained experimentally are in adequacy with the theoretical ones.

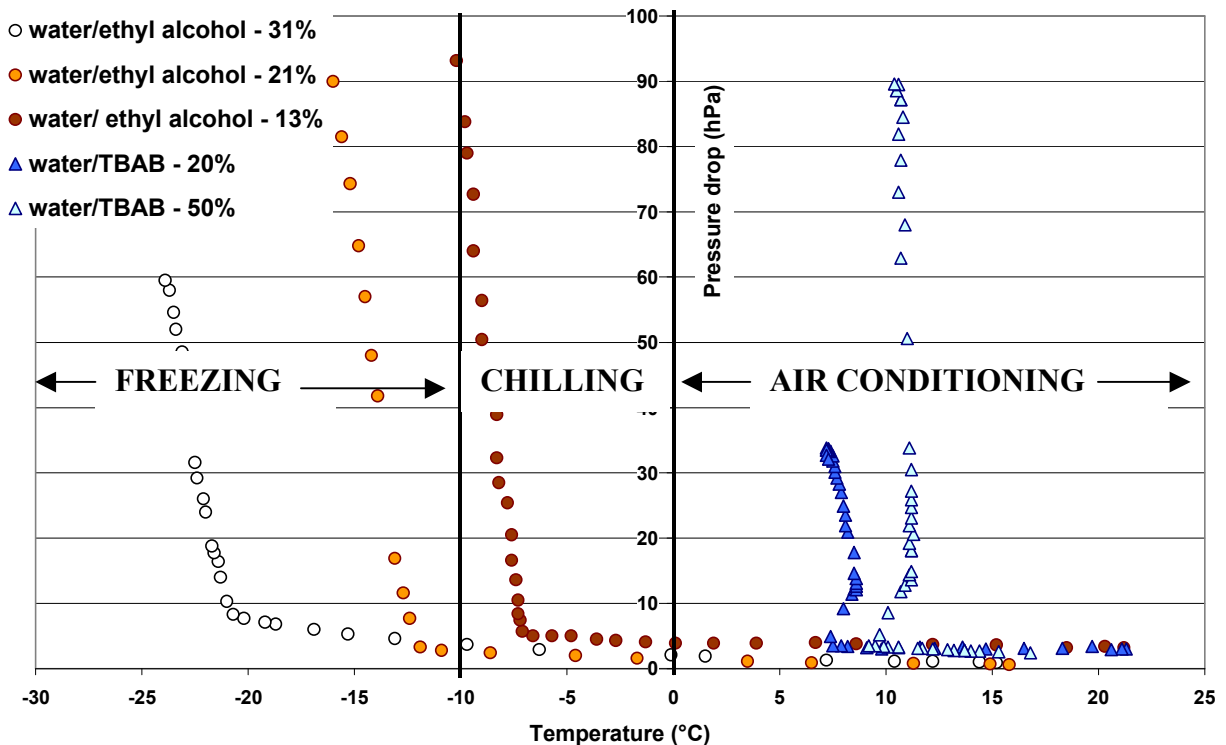


Figure 6 : Pressure drop as a function of the temperature for three different water/ethyl alcohol mixtures and two different aqueous solutions of TBAB.

It is then possible to plot the pressure drop as a function of the ice mass fraction (respectively the hydrate mass fraction) determined with Figure 3 (respectively with Figure 5) for four of the previous selected solutions. Ice slurries of ethyl alcohol (temperature of -5°C) are already employed as secondary refrigerant. For a freezing application, we need to stay in an acceptable range of pressure drop with a sufficient mass fraction of ice (fixed at 20% of ice). We can see in Figure 7 that the slurry obtained with 13% of ethyl alcohol stays in the wished range but, as can be expected, when the rate of ethyl alcohol increases (in order to get a lower freezing point), the viscosity also strongly increases. These results confirm that ethyl alcohol is definitively too viscous for the envisaged application (freezing point at around -25°C).

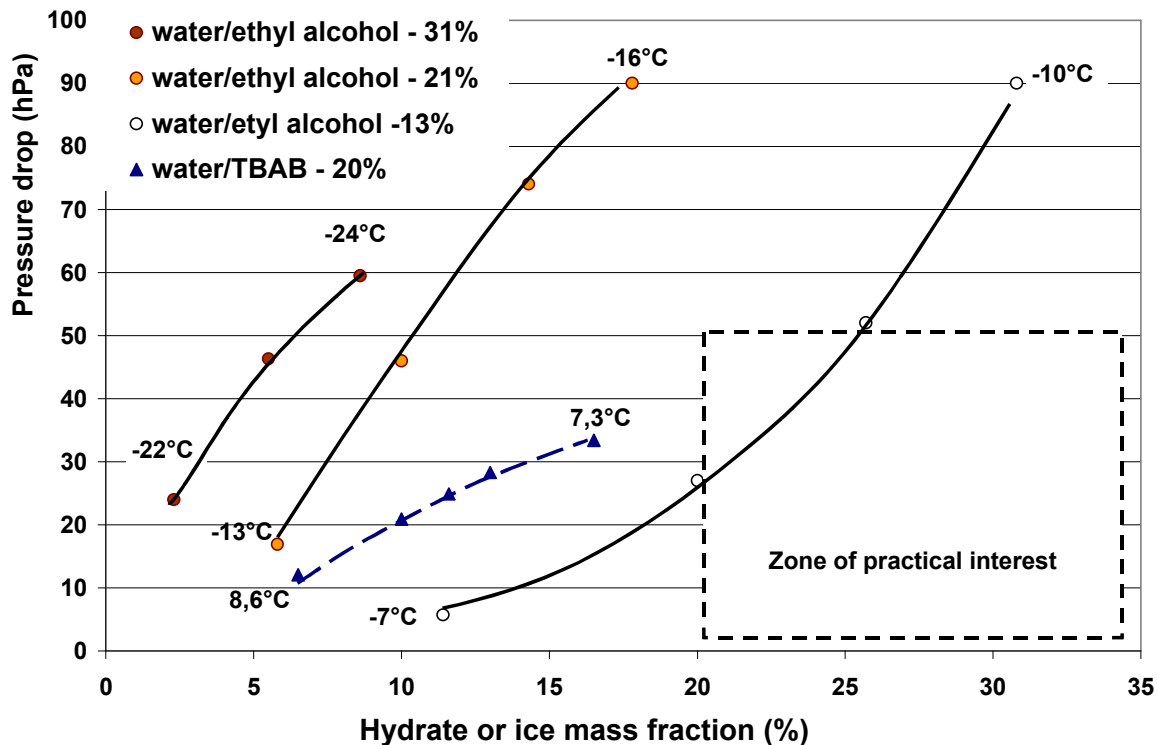


Figure 7 : Pressure drop as a function of the particles mass fraction for three different water/ethyl alcohol mixtures and an aqueous solutions of TBAB.

This is the method we are currently employing to test and compare less viscous candidates for freezer application (for the European Project we are involved in [3]).

Concerning the hydrate slurry, the pressure drop increases less rapidly with the hydrate mass fraction. This result is encouraging as this hydrate slurry could have good transportation properties in secondary loop for air-conditioning.

CONCLUSION

The two phase refrigerant fluids are definitely of great interest thanks to their large cooling capacity. Indeed, ice-slurry at -5°C showed promising results and the challenge is now to develop the technology both at lower temperature (for freezer application), and at higher ones (for air conditioning systems).

The experimental set-up presented can be used in both cases. It was developed to generate and to characterise slurries in a large range of temperature. The examples of ethyl alcohol and TBAB solutions were envisaged in this paper. The ice slurry obtained in the first case is representative of the behaviour of a lot of commonly used refrigerants. When in a two phase state at -35°C , it presents a too high viscosity to ensure an attractive fluid circulation. In the second case, the TBAB shows an interesting example of solution with phase-change temperatures in the range required by air conditioning applications and it confirms that hydrate slurries are potential candidates for such applications.

Candidates for freezing applications are currently studied in the context of an European project; we are also trying to identify hydrate compounds likely to be employed for air conditioning systems. The viscosity specifications are also coupled with toxicological exigencies, with a good cold transport capacity requirement (especially in the hydrate case, where it is wished to find a hydrate slurry with a heat capacity closed to those of ice slurries),

with economical limits,□ which are necessary considerations for the aimed commercial development.

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