International Refrigeration and Air Conditioning Conference

School of Mechanical Engineering

2000

Thermodynamic Properties of Some Currently Used Water-Antifreeze Mixtures When Used as Ice Slurries

O. Lottin
ISITEM Thermokinetics Laboratory

C. Epiard
ISITEM Thermokinetics Laboratory

Follow this and additional works at: http://docs.lib.purdue.edu/iracc

THERMODYNAMIC PROPERTIES OF SOME CURRENTLY USED WATER-ANTIFREEZE MIXTURES WHEN USED AS ICE SLURRIES

Olivier Lottin, Christophe Epiard
ISITEM Thermokinetics Laboratory, UMR CNRS 6607, 44306 Nantes, France

Abstract : cold transport by means of two-phase aqueous secondary refrigerant (mixtures of solid ice and liquid water-antifreeze) makes it possible to use leak-proof and compact refrigerating unit, whereas, thanks to the latent heat of ice, the distribution ducts diameters are kept under reasonable limits. To design efficiently such cold distribution plants, one must know precisely the thermodynamic properties of the slurries, especially the links between the temperature, the ice mass fraction, and the enthalpy. In this paper, we discuss the ways to compute these properties and we give the first results (obtained from already published data and from experiments) for four of the most currently used mixtures.

NOMENCLATURE

c_p	Mass heat capacity	J/kg.K	*Subscripts*	
h	Mass enthalpy	J/kg	a	Antifreeze
L_f	Latent heat of water (0°C)	J/kg	c	Crystallisation
M, m	Mass	kg	e	Enclosure
t	Time	s	l	Liquid phase
T	Temperature	°C	mc	Maximum temperature of crystallisation
x	Mass concentration	kg/kg - (%)	s	Solid phase (ice)
φ	Heat flux	W	i	Initial

1. INTRODUCTION

An increasing number of refrigeration systems are designed with a secondary refrigerant loop, thus reducing the quantity of refrigerant inside the primary plant that can then be leak-proof and compact. However, the secondary refrigerants are often single phase coolant, having a very low heat capacity compared to the primary refrigerant fluids. It is then necessary to considerably increase the mass flow rates, the tubes diameter and the temperature pinches inside the heat exchangers, thus reducing the overall efficiency of the whole systems. One possible way to suppress these unwanted features is to use phase change materials, either liquid-gas mixtures, like CO_2 (Duminil, 1999) or liquid-solid mixtures like ice slurries or stabilised ice slurries (Royon *et al.*, 1999). Liquid-gas mixtures are easy to produce in a usual condenser but due to the high difference between the specific volumes of the two phases, they do not allow cold storage. Liquid-solid mixtures can be employed for cold storage (Christensen and Kauffeld, 1998), but up to now, they still can only be produced by heavy, high-sized and high cost heat exchangers.

Many freezing point depressing agent (antifreeze) can be combined with water and cooled to produce liquid-solid mixtures. However, in order to design efficiently the secondary refrigerant loops, one must know precisely the thermodynamic properties of these mixtures. Although a lot of data concerning the thermophysical properties of single phase secondary refrigerants are available (see for instance the comprehensive work of Melinder, 1997), the thermodynamic properties of biphasic coolant are not so well known.

In the second part of this paper, we introduce a model to compute the thermodynamics properties of the biphasic ice-liquid mixtures that can be easily applied to most of the water antifreeze mixtures thanks to the data published by Melinder. However, we do not know to which extent these data can be used in the case of commercially wide distributed products, as they integrate many additives that may change significantly the properties of the reference mixture. In an attempt to quantify that phenomenon, we determined experimentally the freezing curves of some of the most currently used mixtures and the results are compared to already published ones. The method of measurement is detailed in the third part of the paper and the results are presented in the fourth part.

2. ENTHALPY OF A WATER ANTIFREEZE MIXTURE

The mass enthalpy of the slurry is the sum of the mass enthalpies of the ice and of the liquid mixture at the same temperature T (1) :

$$h_{mix}(T) = x_s.h_s(T) + (1 - x_s)h_l(T,x_{a,l})$$ (1)

The ice mass concentration of the biphasic mixture is a function of the initial antifreeze mass concentration of the mixture $x_{a,i}$ and of the antifreeze mass concentration of the residual liquid, given by the freezing diagram (2) :

$$x_s = 1 - \frac{x_{a,i}}{x_{a,l}}$$ (2)

The mass enthalpies of both pure water and antifreeze in reference state, which means at 0°C and in liquid phase are supposed to be 0 J. Thus, the mass enthalpy of ice can be calculated as follows (3) :

$$h_s(T) = \int_0^T c_{p,s}.dT - L_f$$ (3)

The mass heat capacity of ice is well known. We used the linear equation of Bel and Lallemand recalled below :

$$c_{p,s} = 2,1162 + 0,0078.T$$ (4)

The enthalpy of the liquid phase h_l depends on its antifreeze mass concentration and on the temperature (5) :

$$h_l(T,x_{a,l}) = \left[\int_0^T c_{p,l}.dT\right]_{x_{a,l}}$$ (5)

Theoretically, this model can be applied to every kind of aqueous mixture provided that only water changes of phase and that no chemical reaction occurs between the other components. However, it is still necessary to know precisely the liquid phase heat capacity and its freezing curve on the whole temperature and concentration ranges. The mass heat capacity of the mainly used mixtures of water and pure antifreeze have been determined and published by Melinder. These data are expected to be reliable for the calculation of the thermodynamic properties of the commercially distributed products, when used as a component of a slurry, although these products include some additives : at first because only a slight amount of these additives is added to the liquid antifreeze which may not change significantly its mass heat capacity ; then because the enthalpy of a biphasic water antifreeze mixture is a strong function of the ice mass concentration (through the latent melting heat of ice) and a weak function of the liquid heat capacity. However, the additives may change to some extent the enthalpy of a water antifreeze mixture by changing, even slightly, the shape of its freezing curve which would significantly modify the ice mass concentration of the slurry.

3. FREEZING CURVE OF WATER ANTIFREEZE MIXTURES

These curves were determined in the cases of marketed antifreezes and then compared with those of the corresponding pure products, which are mono ethylene glycol, mono propylene glycol, ethanol and potassium acetate. The water-antifreeze mixture is placed in a cooled enclosure and the changes of temperature of the sample are measured by means of a carefully calibrated Pt 100 probe, while a thermocouple makes it possible to control the temperature of the enclosure. A magnetic stirrer is placed in the sample container. Its roles are to homogenise the temperature field, to prevent the ice from agglomerating close to the walls, and to create disturbances which limit superfusion.

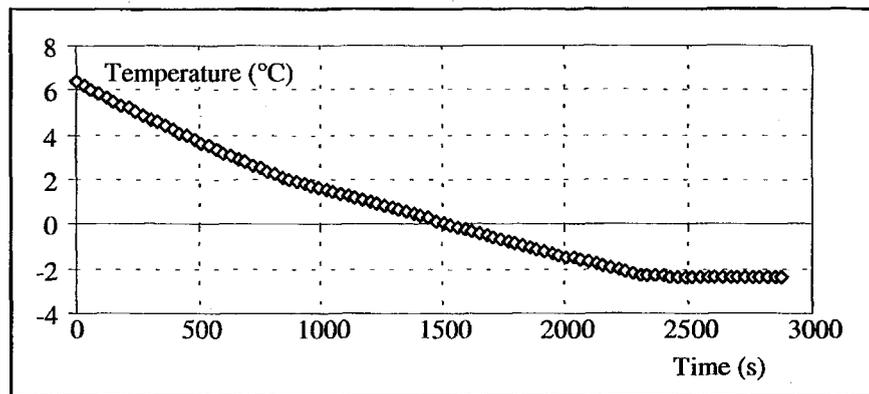## 3.1 First Method : The Superfusion Is Not Taken Into Account

Figure 1 : Measurement of the sample temperature when superfusion does not occur
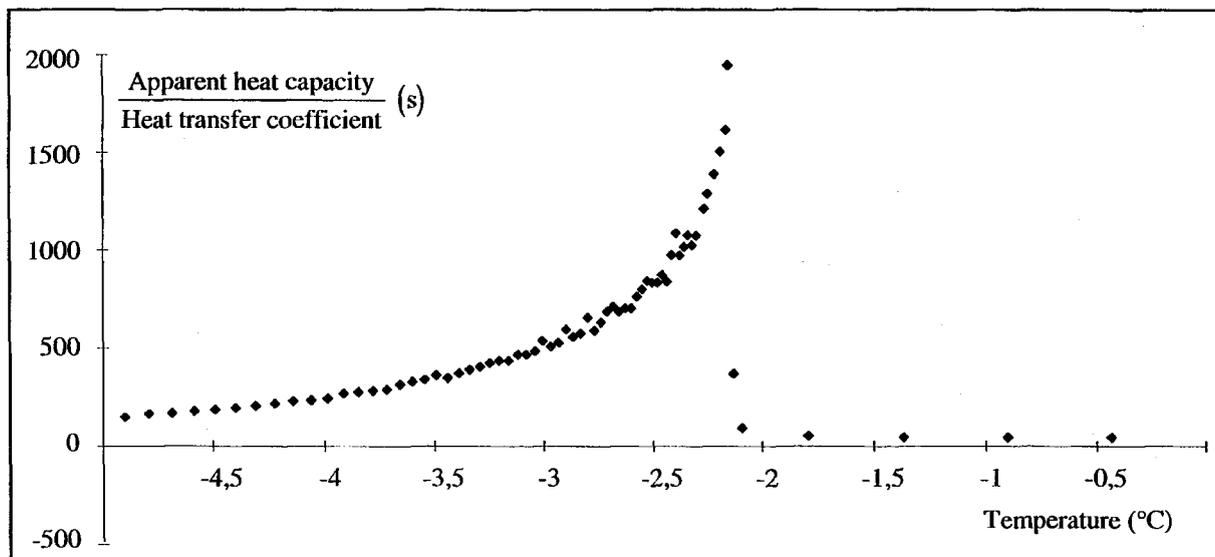

Figure 2 : Measurement of the variation of the ratio between the apparent heat capacity and the total coefficient of heat exchange in a water-antifreeze sample when superfusion does not occur.

When the sample is cooled, its temperature follows a curve whose awaited form is given on figure 1. It is obvious that the freezing of the mixture results in a discontinuity of the curve, whose slope will be less marked on time the phase change starts. This point is however difficult to locate directly, amongst other because the slope of the curve also depends on the difference between the temperature of the sample and that of the enclosure. Generally, the thermal flow lost by the sample can be expressed in two different ways, before the beginning of solidification :

$$\varphi = K.\left(T - T_e\right) = -m.c_{p,l}.\frac{dT}{dt} \tag{6}$$

And after the beginning of solidification :

$$\varphi = K.\left(T - T_e\right) = -\left(m - m_g\right).c_{p,l}.\frac{dT}{dt} - m_s.c_{p,s}.\frac{dT}{dt} + \frac{dm_s}{dt}.\left[h_l(T,0) - h_s(T)\right] \tag{7}$$

K (W/K) is a total coefficient of heat exchange between the sample and the enclosure, which integrates both the convection and conductive transfers. Expressions (6) and (7) can be rewritten as follows :

$$\varphi = K.\left(T - T_e\right) = -m.c_a \cdot \frac{dT}{dt} \quad \Leftrightarrow \quad \frac{\left(T - T_e\right)}{-\dfrac{dT}{dt}} = \frac{m.c_a}{K} \tag{8}$$

In (8), $m.c_a$ is the apparent heat capacity of the single or two phase mixture. By observing the evolution, as a function of the temperature, of the ratio between this apparent heat capacity and the total coefficient of heat exchange K, it is possible in some cases, to locate accurately the freezing point. The curve of figure 2 depicts the measured evolution of the ratio between the apparent heat capacity and the total coefficient of heat exchange when no superfusion is observed. The temperature of the sample decreases gradually (evolution from the right-hand side towards the left while following the points) : the first part of the curve corresponds to an apparent heat capacity equal to the heat capacity of the liquid mixture, which remains constant until the liquid starts to freeze ; when the first crystals of ice appear, the apparent heat capacity increases abruptly which makes it possible to locate the freezing point easily. Then, the value of the apparent heat capacity decreases gradually with the temperature, for tending towards that of a mixture of ice and antifreeze.

3.2 Second Method : The Superfusion Is Taken Into Account

The first method can be rigorous only when no superfusion occurs, which is not always possible, even by agitating the mixture permanently.
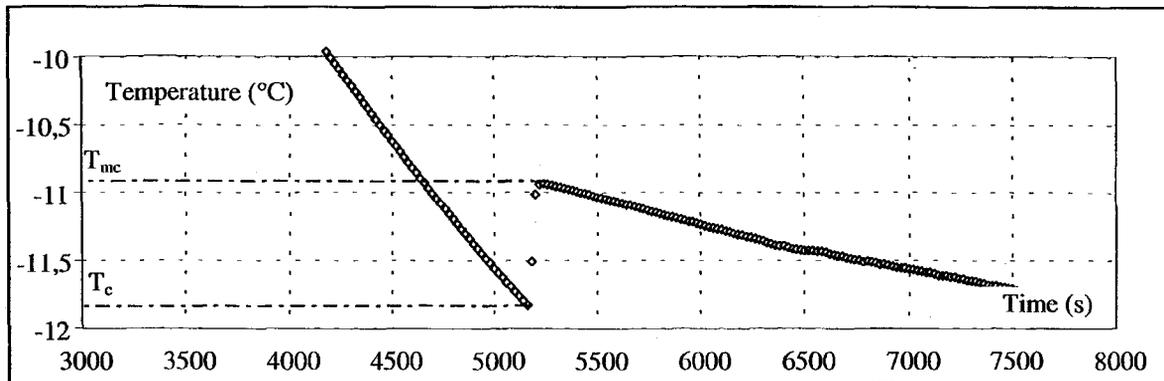

Figure 3 : Measurement of the temperature variation of a water-ethanol sample when superfusion occurs.

The mixture is exposed to superfusion when it is in pure liquid state and when its temperature is lower than the temperature of end of fusion (given by the freezing curve). The breaking of superfusion occurs at the initial temperature of crystallisation (T_c) and results in an abrupt rise of temperature between the point of beginning of crystallisation and the intersection with the liquid solid equilibrium curve. This temperature increase can be regarded as an isenthalpic evolution : it is caused by the formation of a mass of ice, accompanied by the release of latent heat. When no superfusion occurs, the crystallisation temperature (or the temperature of end of fusion of the mixture) is necessarily higher than the maximum temperature observed after the breaking of superfusion (figure 3). In the same way, the antifreeze mass fraction of the liquid phase at the maximum temperature of crystallisation is higher than the initial concentration of the liquid mixture.

The measured evolution of the temperature of a sample exposed to superfusion is shown on figure 3. The evolution of the ratio between the apparent heat capacity and the heat exchange coefficient, as a function of the temperature, appears on figure 4. At first, this ratio remains constant while the temperature goes down (evolution from the right-hand side towards the left on the diagram); then, it becomes negative when crystallisation occurs, which expresses the increase in the temperature of the mixture. It comes back to positive values when the temperature decreases again and follows, together with the concentration, the liquid solid equilibrium curve. The curve of figure 4 makes it possible to determine with a completely satisfactory accuracy the initial freezing temperature T_c and the maximum crystallisation temperature T_{mc}. Once these temperatures known, it is possible to calculate the ice mass fraction of the mixture and the antifreeze mass fraction of the liquid at the maximum

temperature of crystallisation. Considering that the temperature rise which follows the breaking of superfusion is an isenthalpic phenomenon, leads to :

$$M.h_l(T_c, x_{a,i}) = (M - m_s).h_l(T_{mc}, x_{a,mc}) + m_s.h_s(T_{mc}) \tag{9}$$

The ice mass fraction and that of antifreeze in the residual liquid at the maximum crystallisation temperature are given by the following relations (10), which are easily solved in a few iterations :

$$x_s(T_{mc}) = \frac{m_s}{M} = \frac{h_l(T_c, x_{a,i}) - h_l(T_{mc}, x_{a,mc})}{h_s(T_{mc}) - h_l(T_{mc}, x_{a,mc})} ; \quad x_{a,mc} = x_{a,i} \cdot \frac{h_s(T_{mc}) - h_l\left(T_{mc}, \dfrac{x_{a,i}}{1 - x_s}\right)}{h_s(T_{mc}) - h_l(T_c, x_{a,i})} \tag{10}$$
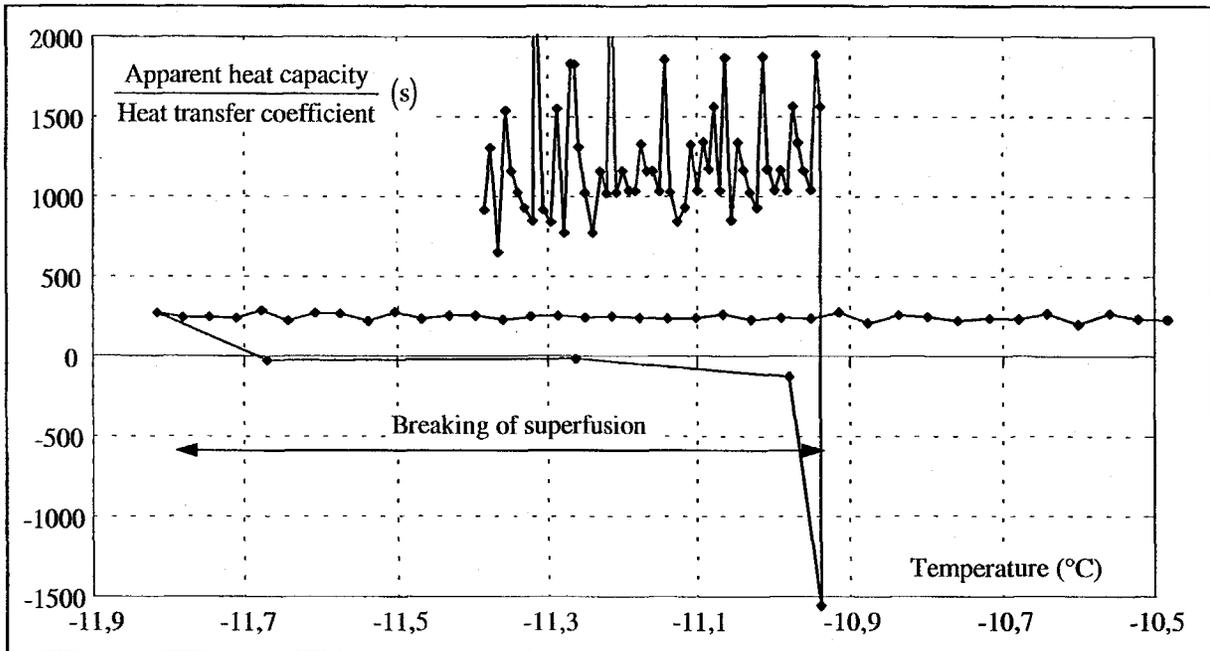

Figure 4 : Measurement of the variation of the ratio between the apparent heat capacity and the total coefficient of heat exchange in a water-ethanol sample when superfusion occurs.

3.3 Validity Of The Second Method

The Pt 100 probe which was used for measurements was calibrated with a precision of 0,03°C. When superfusion is not very pronounced, the differences between the end and the initial temperatures of crystallisation can be lower than 0,2°C. In this case, an error analysis applied to relation (10) shows that the relative inaccuracy concerning $x_{a,mc}$ is lower than 0,15 %. In practice, it was always noted that for weak superfusions, the results tended towards those obtained by the direct method. Moreover, the dispersion of the points is not more significant : in the case of three different antifreezes not very prone to superfusion, the first 4 and even 5 decimals of the freezing curve coefficient of correlation R^2 were identical when one or the other of the methods were applied. Under our conditions of measurement, the method of taking into account the superfusion by application of relation (10) can thus be regarded as valid when this one is not very marked.

When the superfusion is more pronounced and reaches a few degrees, a problem arises linked to thermal inertia of the Pt 100 probe (Ø 3 mm). The temperature increase related to the breaking of superfusion is indeed a quite short phenomenon (it lasted about one minute in our conditions of test, the total volume of mixture being about 0,2 l). To try to quantify the inaccuracy dependent with the probe response time, tests were carried out using a not

insulated thermocouple, the welding of which can be considered as a 1 mm sphere. This thermocouple was calibrated to give an identical value to that of the Pt 100 : in practice, one observes an absolute residual variation of about 0,015 °C, related to signal fluctuations. This variation is not significantly modified during the cooling of the sample. On the other hand it increases during the phase of breaking of superfusion, provided this one is of a sufficient amplitude, to reach maximum values lower than 0,2°C. An error analysis applied to the relation (10) indicates then that the relative inaccuracy on $X_{a,mc}$ is lower than 0,60 %. In fact, the use of the thermocouple in our case led to a greater dispersion of the results which were affected by the signal fluctuation : thus the tests were always carried out using the thermistor and the accuracy was considered as satisfactory.

4. RESULTS AND DISCUSSION

The freezing curves of the antifreezes were measured between 0°C and -15°C. Measurements were systematically interpreted in two different ways : without taking account and by taking account of superfusion. In practice, superfusion could be avoided only very seldom : when it was not taken into account, the temperature of end of crystallisation was considered equal to the temperature of phases equilibrium for an antifreeze mass fraction equal to the initial concentration. When superfusion was met, it was always considered independently of the difference between the temperature of beginning and that of end of crystallisation, even when this difference was very low. Two experimental curves were thus obtained for each antifreeze. The data were correlated in the form of degree 3 polynomials, whose coefficients are given in table 1. For simplicity reason, and considering that the temperature ranges were small, the data from other authors were correlated similarly. Comment are quickly made about the shape of the curves but they are not shown in this paper.

4.1 Freezing Curves

Table 1 : Coefficients of the freezing curves interpolation polynomials.

		x	x^2	x^3	R^2
Ethanol	**Not considering superfusion**	-0,36838426	-0,00349378	-0,00021549	0,999
	Considering superfusion	-0,36015496	-0,00525292	-0,00007594	0,998
	Guilpart *et al.* (1999)	-0,36838426	-0,00349378	-0,00021549	1,000
Potassium acetate	**Not considering superfusion**	-0,16885223	-0,00170287	-0,00001472	0,996
	Considering superfusion	-0,16796847	-0,00177932	-0,00001424	0,996
	Melinder (1997)	-0,20350700	0,00074087	-0,00004764	1,000
MEG	**Not considering superfusion**	-0,27799839	-0,00321576	-0,00006706	0,999
	Considering superfusion	-0,28390354	-0,00277992	-0,00007688	0,999
	Melinder (1997)	-0,28319950	-0,00360933	-0,00010498	1,000
MPG	**Not considering superfusion**	-0,23992143	-0,00274045	-0,00008721	0,999
	Considering superfusion	-0,23959857	-0,00268310	-0,00008781	0,999
	Melinder (1997)	-0,28439758	-0,00164997	-0,00010861	1,000

The ethanol we used for measurements is a superfine 95° denatured ethanol. It is thus not a pure product and the measured freezing curves are logically a little above the curve resulting from theoretical data. For this one, we chose the data of Mellan (1970), correlated by Guilpart (1999). It should be noted that the results of different authors diverge always slightly and that we would not have obtained the same curve starting from the data of Melinder. The discrepancy between the coefficients of the two experimental curve shows that, under our conditions of measurements, ethanol was always prone to a rather significant superfusion : the difference between the initial and the maximum temperatures of crystallisation reached 2,7°C.

The antifreeze based on potassium acetate that we used is, under identical experimental conditions, much less prone to superfusion than ethanol, as show the coefficients of the experimental curves which are close to each other. During the measurements, the most significant variation between the initial and the maximum temperature of crystallisation was 0,55°C. According to the manufacturer, the potassium acetate mass fraction of the tested antifreeze equals 46,5 % : the coefficients of table 1 have been calculated, according to this value and to the data of

Melinder. This gives a curve which is close to the experimental ones but the discrepancy is minimised when the potassium acetate mass fraction equals 47,6 %.

The antifreezes containing MPG and MEG that we tested are not pure products and the experimental curves are thus above the curves of Melinder. The manufacturer indicates that the MEG mass fraction of its antifreeze is between 91 and 95 %. Indeed, the correction of Melinder' curve so that it is closest to the experimental one (with taking into account of superfusion) gives a MEG mass fraction of 93,5 %. The antifreeze containing MEG we tested was not very sensitive to superfusion. The maximum difference observed between the initial and the maximum freezing temperatures was about 0,5°C. Like MEG, MPG is not very prone to superfusion and the maximum difference between the two temperatures of crystallisation is 0,6°C. The discrepancy between theoretical and experimental curves is minimised for an antifreeze MPG mass fraction equal to 95,3 %, whereas the manufacturer indicates that this value is between 90 and 94 %.

4.2 Application Fields
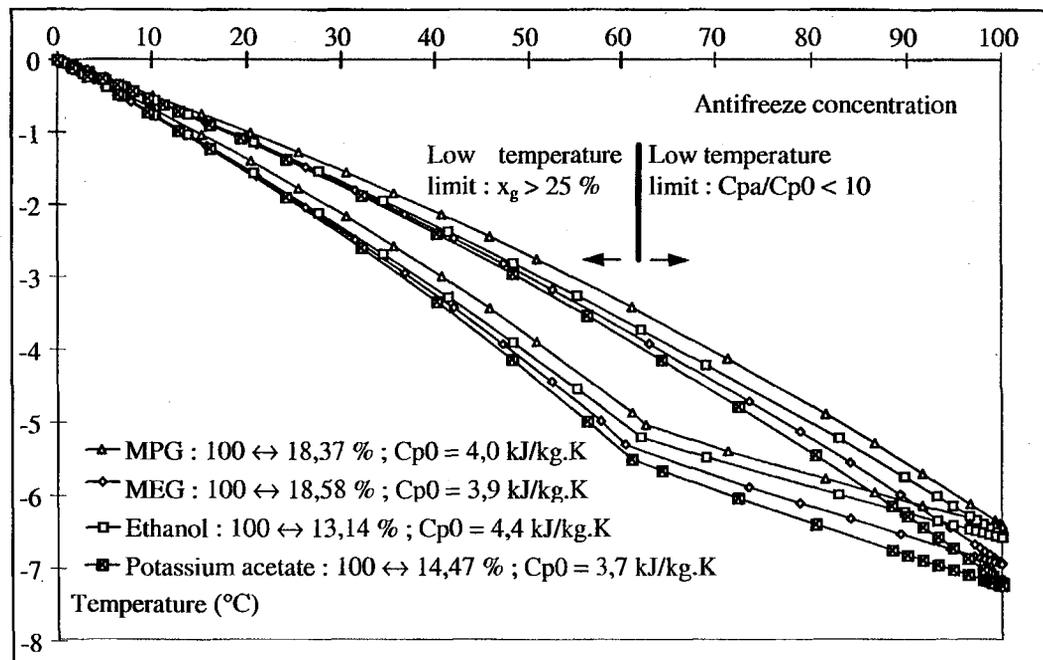

Figure 5 : Temperature - concentration fields inside whose $x_s < 25$ % and $Cpa/Cp0 > 10$.

To see if the behaviours of various antifreezes could be qualitatively different, we plotted on figure 5 the limits of the fields inside whose the ratio between the apparent heat capacity of the two phase mixture and the real heat capacity of the single phase mixture at 0°C is higher than a value arbitrarily fixed to 10. Furthermore, at the lower concentrations, these fields are limited by the ice mass fraction whose maximum value was fixed to 25 % : this value was selected because it can be regarded as the highest ice mass fraction allowing the transport of the slurries by the usual means of pumping. The antifreeze mass fraction of the mixtures were all corrected so that the lowest temperature point corresponds to a concentration of 100. One notices immediately that for freezing temperatures ranging between 0°C and -5°C, the temperature range inside of which the ice mass fraction lies between 0 % and 25 % is very narrow : consequently, a simple temperature measurement cannot be a good indicator of the ice mass fraction of the mixture. This range of temperature widens when the initial antifreeze mass fraction increases and when the freezing temperature decreases. Figure 5 also shows that the behaviour of the four tested antifreezes are qualitatively identical and that, determined this way, their application fields are of similar width : only the antifreeze quantity that was necessary to reach the lowest temperature point differentiates them. This quantity is lower in the case of ethanol, which has also, when mixed with water, a higher mass heat capacity than that of the other antifreezes.

4.3 Enthalpy Variations

As for any phase change materials, the mass enthalpy variation of a slurry can be very significant on small temperature ranges. Table 2 show the enthalpy variations of the four mixtures when the ice mass fraction varies between 0 % and 20 %. Once again, the four mixtures behave in a qualitatively identical way. The highest variations are obtained with ethanol, but the relative differences between ethanol and the other antifreezes are lower than 10%. One can see that the enthalpy variations, as well as the temperature range inside which the ice mass fraction lies between 0% and 20 %, increase with the antifreeze concentration of the mixture.

Table 2 : Enthalpy variations of the water-antifreeze mixtures.

Antifreeze mass concentration (% by weight)		5	10	15	20	25	30
Ethanol (95 °)	Δh (kJ/kg)	68,4	70,1	72,4	75,7	79,1	79,3
	Freezing T. (°C)	-1,9	-4,2	-6,9	-9,9	-13,5	-17,6
	Temperature at $x_s = 20\%$ (°C)	-2,5	-5,4	-8,4	-13,5	-18,9	-24,2
MEG (91 - 95 % by weight)	Δh (kJ/kg)	67,9	69,1	70,6	72,8	75,3	76,8
	Freezing T. (°C)	-1,5	-3,1	-5,1	-7,4	-10,0	-13,0
	Temperature at $x_s = 20\%$ (°C)	-1,9	-4,1	-6,8	-10,0	-13,9	-18,1
MPG (90 - 94 % by weight)	Δh (kJ/kg)	67,9	68,9	70,5	72,8	76,4	79,2
	Freezing T. (°C)	-1,3	-2,7	-4,5	-6,6	-9,0	-12,0
	Temperature at $x_s = 20\%$ (°C)	-1,6	-3,6	-6,0	-9,0	-12,9	-17,2
Potassium acetate (46,5 % by weight)	Δh (kJ/kg)	67,5	68,1	68,8	69,6	70,7	72,2
	Freezing T. (°C)	-0,9	-1,9	-3,0	-4,1	-5,4	-6,9
	Temperature at $x_s = 20\%$ (°C)	-1,1	-2,4	-3,8	-5,4	-7,2	-9,3

5. CONCLUSIONS

The method of measurement which was used is based on the taking into account of superfusion for the detection of freezing points of water antifreeze mixtures and the determination of their freezing curve. This method gives good results whatever the degree of superfusion : it makes it possible to avoid the problems caused by a strong superfusion and it also makes it possible to detect easily and accurately the freezing temperature of mixtures which are not very prone to superfusion. The results show that in some cases, like that of ethanol, superfusion must absolutely be taken into account if the freezing point temperature is measured during the cooling of the mixture. This study of some aqueous solutions is not exhaustive and it was not possible to highlight a qualitative difference concerning the behaviour of various antifreezes. It appears that the apparent heat capacity of the mixtures is high only for temperatures close to the freezing point. Moreover, when the antifreeze mass concentration is low, the temperature ranges are limited rather by the maximum ice mass fraction of the mixture than by the apparent heat capacity. The results showed that it was possible to use previously published data, although established for pure substances, to calculate the thermodynamic properties of more complex products.

REFERENCES

Bel O., Lallemand A., 1999a, Etude d'un fluide frigoporteur diphasique ; 1 : caractéristiques thermophysiques intrinsèques d'un coulis de glace, International Journal of Refrigeration, Vol. 22, pp. 164-174.

Christensen K. G., Kauffeld M., 1998, Ice slurry accumulation, proceedings of IIR Gustav Lorentzen Conference "natural working fluids", pp. 701-711.

Duminil M., 1999, Le CO_2 comme frigoporteur diphasique, Revue Générale du Froid, N° 994, pp. 29-37.

Guilpart J., Fournaison L., Ben Lakhdar M. A., 1999, Calculation method of ice slurries thermophysical properties - application to water/ethanol mixture, proc. 20th Int. Congress of Refrigeration, Sydney, Australia.

Melinder A., 1997, Thermophysical properties of liquid secondary refrigerant, published by the International Institute of Refrigeration.

Mellan I., 1970, Industrial solvents handbook, Noyes Data Corporation, New Jersey, USA.

Royon L., Perrot P., Colinart P., Guiffant G., 1999, Transport of cold thermal energy with a new secondary biphasic refrigerant : the stabilized ice slurry, proc. 20th Int. Congress of Refrigeration, Sydney, Australia.