

FREEZING POINT DEPRESSION OF VARIOUS ICE SLURRIES

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ABSTRACT

Ideal solutions with equal molar concentration have an equal freezing point. The properties that determine heat and mass transfer processes encountered in a secondary cooling cycle are however determined by the mass fraction of solutes. Generally for aqueous solutions, the more freezing point depressant added, the less efficient heat and mass transfer properties. Therefore substances with low molecular weight are expected to result in more efficient ice slurries.

By calculating ice slurry properties, heat transfer and pressure drop, it was investigated if ice slurries of low molecular weight additives result in efficient ice slurries. For the substances considered, it was found that the molecular weight is a good indication for ice slurry efficiency, but is not decisive under all conditions. Ice slurries of three particular substances were found to have most promising properties: Sodium chloride, lithium chloride and potassium formate.

Substances like antifreeze proteins depress the freezing point of a solution actively by interfering in the ice crystal formation. These substances have been suggested for freezing point depression in ice slurries too, but can only be used to control ice crystal size or supercooling effects, and not to depress the freezing point because of the extra temperature difference introduced with thermal hysteresis.

1. INTRODUCTION

Ice slurries are increasingly applied as the working fluid in secondary cooling systems in supermarkets, in air-conditioning and in other applications. The secondary cycles are installed to benefit from advantages of load shifting and peak load levelling. Also safety hazards involved with primary refrigerants as ammonia or hydrocarbons can be reduced or avoided by applying secondary cooling cycles.

Efficiency of ice slurries as working fluid in secondary cooling cycles is high because of the use of the latent heat of the ice/water phase change, rather than using only the sensible heat effect involved with a temperature change of a brine. Heat transferred to an ice slurry melts a small amount of ice instead of increasing the temperature without phase change. Cold is stored and transported at high density and pipe diameters and storage vessels can be small. Until now the main disadvantage has been the expensive ice slurry generator needed for producing the ice slurries.

Ice slurries consist of a water solution with small (0.01 mm-0.1 mm diameter) ice particles. By addition of a substance that depresses the freezing point, ice slurries can be produced from just below 0 °C down to -20 °C or at even lower temperatures. Many different substances can be used to depress the freezing point. All substances also alter thermophysical properties of the solution, which determine heat and mass transfer properties. In previous work (Meewisse and Infante Ferreira, 2000) it was shown that the ice fraction for a great part determines the efficiency of the ice slurry produced, but that the choice of freezing point depressant also is of considerable importance.

Recent investigations (Frei and Egolf, 2000) have shown that apart from the ice fraction also size and shape of ice crystals influences ice slurry mass and heat transfer properties considerably.

Because of recrystallisation ice crystals are continuously changing size and shape during storage or under stress. Freezing point depressing substances can also interact in these processes. Traditional freezing point depressants do not directly influence size and shape of ice particles, only indirectly by altering heat and mass transfer rates during ice formation. A different type of substances does interfere actively with the ice formation, for example antifreeze proteins, suggested for ice slurries by Grandum and Nakagomi (1997).

This paper discusses the ways the freezing point depressing substances can be applied to increase efficiency of ice slurries. Efficiency of freezing point depressants that depress the freezing point in a colligative manner are compared quantitatively. It is evaluated whether or not the properties that result in efficient freezing point depression also lead to high performance in practical ice slurries. Effects of using other freezing point depressants are discussed qualitatively, as not many data are available yet for these substances.

2. FREEZING POINT DEPRESSION

The freezing temperature (T_f) of an ideal solution can be estimated with:

$$T_f = \frac{1}{\frac{1}{T_0} - \frac{R \cdot \ln(a_w)}{\Delta h_f \cdot M_w}} \quad (1)$$

where R is the gas constant, Δh_f the enthalpy of fusion and a_w the activity of water, which depends on molecular weight of solute and water (M_i and M_w) and the solute fraction (w_i):

$$a_w = \frac{1}{1 + \frac{w_i \cdot M_w}{(1 - w_i) \cdot M_i}} \quad (2)$$

Equation (1) can be derived from the Clapeyron equation using Raoult's law. In Equation (1) it is assumed that the latent heat of fusion is independent of temperature. The prediction of the freezing point of a mixture is only valid for dilute solutions and for freezing point depressants with little interaction with water molecules, because it ignores interactions between solute molecules and it ignores specific interactions with water caused by various molecular properties as polarity, ion charge and other properties. In Equation (1), freezing temperature of a solution is proportional to the molality of the solution. Solutions with equal molality have equal freezing point depression. The freezing point is determined by the number of molecules only and is a colligative property.

The performance of an ice slurry in a secondary cooling system is not only determined by the freezing point depression and the ice fraction, but for a great part also by mass and heat transfer properties as heat capacity, viscosity, density and thermal conductivity. For aqueous solutions these properties become less efficient when more solute is added. Mostly this is not in a proportional way to the molar fraction as is approximately the case with the freezing point depression. An equal mole fraction of a similar solute will result in equal freezing points but not in an equal viscosity of the solution. Solutes with a low molecular weight therefore probably result in more efficient ice slurries compared to similar components with higher molecular weight that form solutions of equal freezing point. In order to test if this applies in practice, pairs of similar substances were compared: Methanol and ethanol, sodium chloride and lithium chloride, ethylene glycol and propylene glycol. Also potassium formate was compared, because it consists of relatively small molecules and has

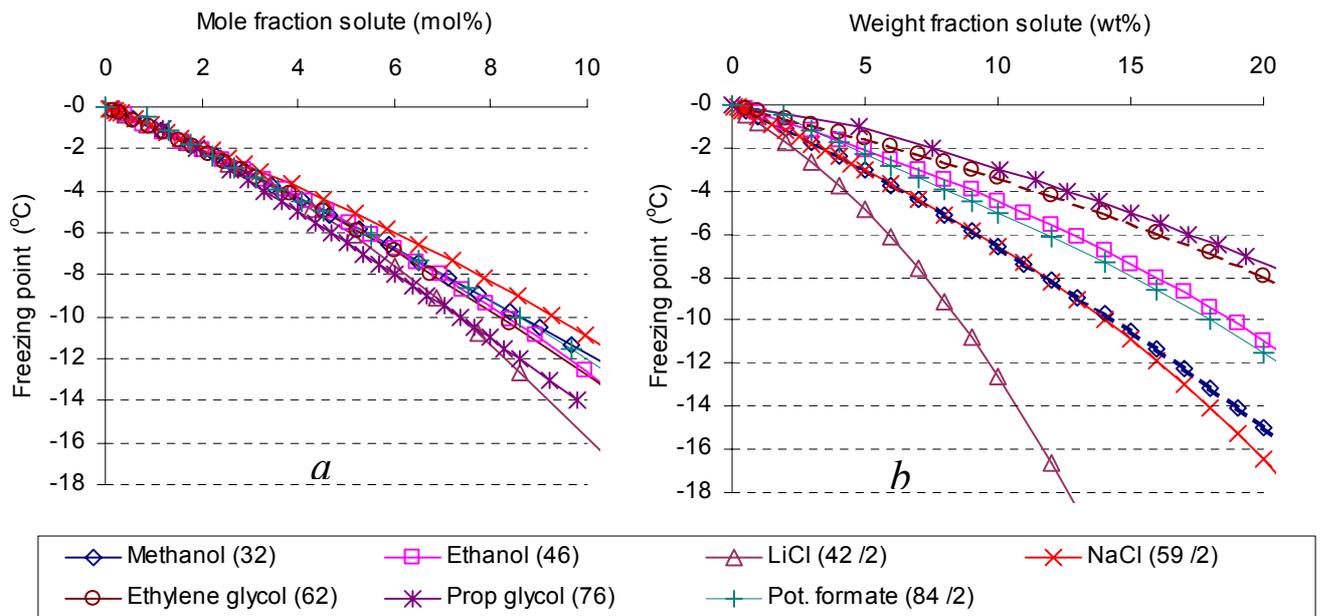


Figure 1, Freezing Point vs. Mole Fraction (a) or Weight (b). (Molecular weight in parentheses)

good properties as a secondary refrigerant without phase change.

Indirect effects of interactions of the freezing point depressants with the ice formation, and therefore with the thermophysical properties that are determined by size and shape of ice particles, are not compared quantitatively. Effects on the carrier fluid are calculated with data available from various references (Melinder 1997, CRC Handbook).

In Figure 1 (a) the freezing temperatures of the different solutions are shown versus the molar fraction. Especially at low mole fraction freezing curves are almost equal. In Figure 1 (b) the same curves are displayed versus the mass fraction. Starting point of all curves is the origin, but the curves of the low molecular weight components are lower. This means these components require low amounts of additive to get an ice slurry of a certain temperature. Thermophysical properties like viscosity and heat conductivity will be better than for the components with higher freezing curves.

If the apparent heat capacity is also higher is not certain. Since the lower freezing curves have equal starting points, the slope of the curves is steeper, which is a negative effect for the cold storage capacity of the ice slurry. Ice consists of pure water, the solute concentration in the remaining liquid phase will increase upon an increase of the ice fraction. A small additional freezing point depression is the result and the ice slurry needs to be cooled an additional part along the sensible heat capacity, rather than with the latent heat of fusion, see also Figure 2. This decreases the efficiency of the ice slurry. This effect is the reason why the advantage of ice slurries reduces at lower temperatures: Freezing curves are steeper and sensible heat effects are relatively more important.

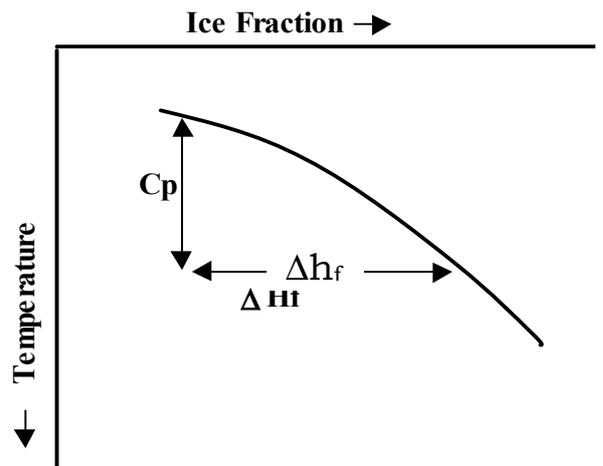


Figure 2, Latent Heat versus Sensible heat on the Freezing Curve of a Solution

3. THERMOPHYSICAL PROPERTIES OF ICE SLURRIES

Methods to calculate density, viscosity, heat conductivity and apparent heat capacity are given here. *Density* of ice slurries is obtained by volume weighted addition of the density of pure ice and the density of the solution. Densities of solutions are available from literature (Melinder 1997, Soehnel 1985).

Ice slurries have Newtonian flow behaviour up to ice concentrations of 15% to 25%, depending on the type of ice slurry or depending on the error margin tolerated. For Newtonian fluids, the ice slurry *viscosity* (η_{is}) can be estimated from the Thomas correlation, used by Bel and Lallemand (1999) and Kauffeld et al, for ice slurries, with η_l the liquid viscosity and w_s the ice weight fraction:

$$\eta_{is} = \eta_l \cdot (1 + 2.5 \cdot w_s + 10.05 \cdot w_s^2 + 0.00273 \cdot e^{16.6 \cdot w_s}) \quad (3)$$

Theoretical investigations by Ben Lakhdar (1998) have shown that the model proposed by Tareef for *heat conductivity* of two phase mixtures, yields satisfactory results for ethanol ice slurries up to an ice mass fraction of 0.4. A direct method to test ice slurry heat conductivity is still lacking, but results of the Tareef method agree with other models and can therefore be used for calculations in this work:

$$\lambda_{is} = \lambda_l \cdot \left(\frac{2 \cdot \lambda_l + \lambda_s - 2 \cdot w_s \cdot (\lambda_l - \lambda_s)}{2 \cdot \lambda_l + \lambda_l + w_s \cdot (\lambda_l - \lambda_s)} \right) \quad (4)$$

The ice slurry *heat capacity* is found by differentiation of enthalpy (h) with respect to temperature, which yields:

$$c_{p_app} = \left(\frac{dw_s}{dT} \right) \cdot [h_s - \Delta h_f - h_l] + w_s \cdot c_{p_s} + (1 - w_s) \cdot c_{p_l} \quad (5)$$

The heat capacity is an *apparent* heat capacity (c_{p_app}), because apart from the sensible heat effects it also contains a part describing the heat effect of the phase change, the first term of Equation 5. The enthalpy change for ice formation (ΔH_f) is a weak function of temperature, but is considered constant here. Enthalpies and heat capacities of pure ice and liquid solutions are obtained from literature.

4. CRITERIA FOR ICE SLURRY PERFORMANCE

Thermophysical properties of ice slurries made of various freezing point depressants were evaluated for performance in secondary cooling with typical correlations known for ice slurry systems, including heat transfer and pressure drop. Typical operating conditions were estimated, a complete evaluation of different operating conditions was not included in this work.

To estimate turbulent heat transfer coefficients for ice slurries, various researchers (Knodel et al., 2000, Kauffeld et al., 1999) have proposed to use a well known equation for prediction of a Nusselt number for the carrier fluid, and modify this number with an extra term that includes the ice fraction. In the research of Kauffeld the Reynolds number is included in this extra term. In the work of Knodel the Nusselt number for the liquid is multiplied at higher ice fractions than 4% with a constant of value 0.885. If correlations of this form are valid, ice slurries produced from additives that also form efficient secondary refrigerants without phase change will be more efficient. Indirect influences of the ice on the thermophysical properties of the ice slurry however are disregarded with

this method. Therefore it is more accurate to use ice slurry properties directly in a correlation for the Nusselt number.

Turbulent flow conditions are most often encountered in the ice slurry generator. Turbulent heat transfer strongly depends on the type of heat exchanger. Some researchers have presented correlations for scraped surface heat exchangers (Bel and Lallemand, 1999), for vacuum machines (Zakeri, 1997), for fluidised bed systems (Meewisse and Infante Ferreira, 1999) and for others. Most correlations include Reynolds ($Re = \rho v D / \eta$) and Prandtl ($Pr = \eta c_p / \lambda$) dimensionless numbers and follow the general form of Equation (6):

$$Nu = c \cdot Re^x \cdot Pr^y \quad (6)$$

Equation (6) can also be extended with a term that includes the ice fraction. In this work this term was however disregarded as it does not influence the choice of freezing point depressant. The data for c , x and y of Dittus and Boelter were used in the comparison, 0.027, 0.8 and 0.33 respectively. The comparison does not yield exact data, but are only used for comparison purposes.

During transport, storage and often in application stages of a secondary cooling system, laminar flow conditions are likely. A heat transfer correlation for laminar flow conditions has been proposed by Guilpart et al. (1999) after experiments with ethanol type ice slurries:

$$Nu = 38.3 \cdot Gz^{0.15} \cdot w_s^{0.52} \quad (7)$$

where Gz is the Graetz number ($\pi Re Pr D / 4z$), with z the distance in the tube (m).

The size of piping and storage vessels is mainly determined by the amount of cold that can be stored in a vessel or transported through a tube. The apparent heat capacity is the only thermophysical property that determines this.

Another factor is the additional power input that is required for pumping of the ice slurry and for agitation of the ice slurries in storage vessels. Pumping power required can be estimated from pressure drop, given by

$$\Delta p = 2 \cdot f \cdot \rho \cdot v^2 \cdot L / D \quad (8)$$

where f is the friction factor, for laminar flow conditions given by $f = 16 / Re$. For turbulent conditions f is estimated with the Blasius equation: $f = 0.08 / Re^{0.25}$. Equation (8) disregards effects of non-Newtonian flow behaviour at higher ice fractions, but can be used for a comparison of substances. Power input (P) for agitation of ice slurries in storage vessels can be estimated with the Power number ($N_p = P / D^5 \cdot N^3 \cdot \rho$):

$$N_p = K \cdot Re^a \cdot Fr^b \quad (9)$$

with Re the Reynolds number ($D^2 \cdot N \cdot \rho / \eta$), Fr the Froude number ($D N^2 / g$) where D is the vessel diameter and N the agitator speed in revolutions per second. K , a and b are constants depending on geometry and conditions in the storage vessel. Under laminar flow conditions a tends to 1 and the stirring power becomes proportional to the viscosity. Under turbulent flow conditions a and b tend to zero and stirring power input depends only on the density of the ice slurry. In ice slurry vessels laminar flow conditions are more likely, especially at higher ice fractions, so stirring power input is determined by the ice slurry viscosity.

During transport and storage of ice slurries heat transfer rates should be as low as possible. This can be achieved much easier by insulation and improved process conditions, than by modification of thermophysical ice slurry properties as the freezing point.

5. COMPARISON

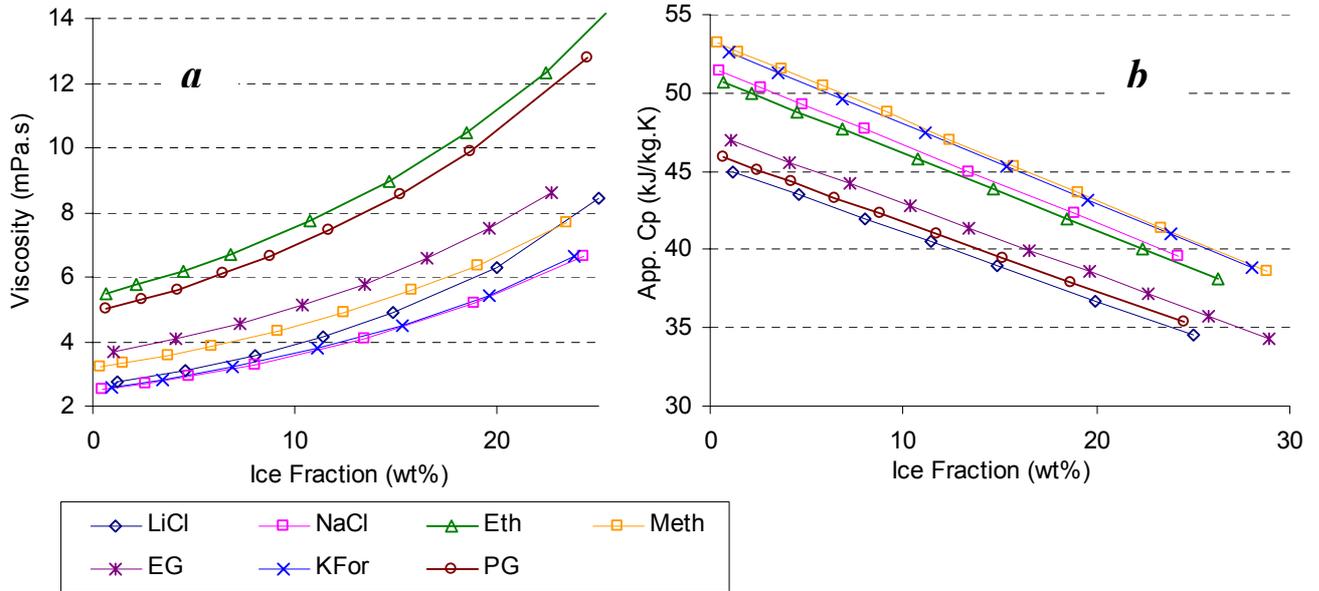


Figure 3, Viscosity (a) and Apparent heat capacity (b) of Ice Slurries at -6°C

In Figure 3(a) viscosity of ice slurries at -6°C is displayed, which is an important property for heat and mass transfer processes, and solely determines power consumption required for agitation of ice slurries in storage vessels. Low viscosities are advantageous for heat transfer rates and power consumption. Methanol ice slurry has lower viscosity than ethanol, ethylene glycol (EG) has lower than propylene glycol (PG). Lithium chloride however, has equal or higher viscosity than sodium chloride. Potassium formate (KFor) also has low viscosity.

In Figure 3(b) apparent heat capacities are displayed at -6°C . This property determines size of storage vessels and tubing equipment. The apparent heat capacity is mainly determined by the ice fraction, still there is up to 20% variation between different freezing point depressants. Sodium chloride, methanol and potassium formate have the highest values.

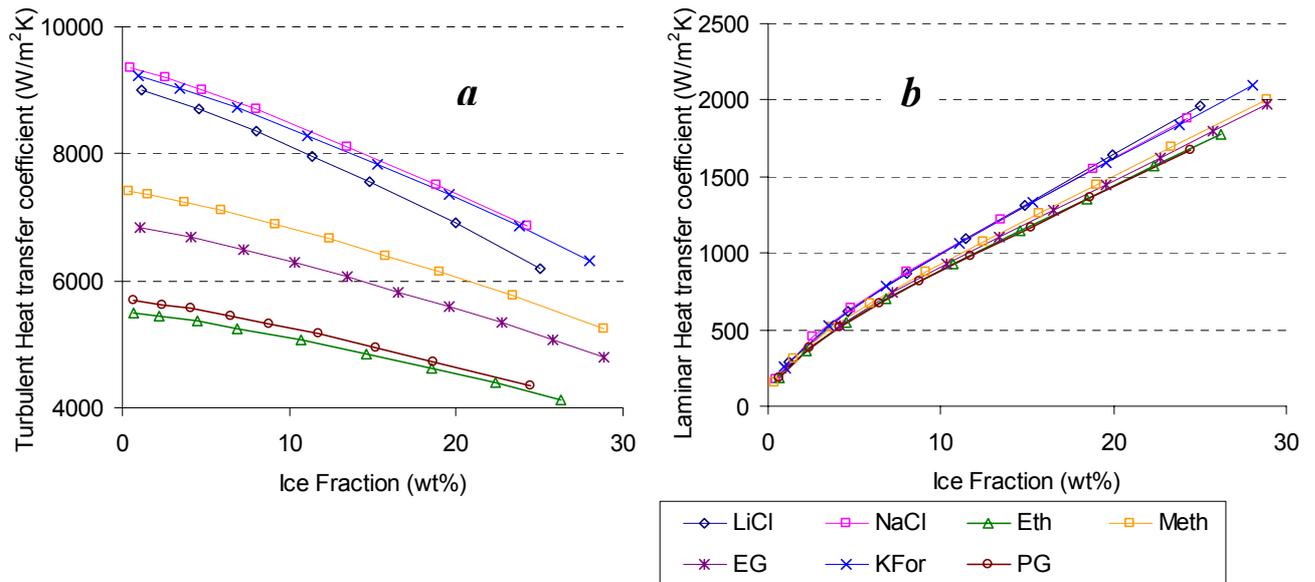


Figure 4, Heat transfer coefficients for turbulent flow conditions ($v=2\text{ m/s}$, (a)) and for laminar flow conditions ($v=0.3\text{ m/s}$ (b)) at $-6\text{ }^{\circ}\text{C}$, $D=0.02\text{ m}$.

In Figure 4(a) heat transfer coefficients are shown versus ice fraction for turbulent conditions in a heat exchanger with ice slurry velocity of 2 m/s and tubing diameter of 0.02 m at a temperature of $-6\text{ }^{\circ}\text{C}$, a temperature required in cooling applications. The curves have been determined with the model of Equation (6).

Heat transfer of methanol is higher than that of ethanol and heat transfer of ethylene glycol (EG) is higher than for propylene glycol (PG). The heat transfer of lithium chloride however is not higher than that of sodium chloride. The apparent heat capacity of lithium chloride is much lower than for sodium chloride. The freezing curve of lithium chloride of Figure 2 therefore does not result in very efficient heat and mass transfer properties at this temperature. An overview of thermophysical properties and performance data is given in Table 1 for ice slurries with 10 wt\% of ice at $-6\text{ }^{\circ}\text{C}$. Though sodium chloride has higher heat transfer than lithium chloride, lithium chloride still has a high heat transfer when compared to the other substances. Also potassium formate has high heat transfer.

In Figure 4(b) heat transfer coefficients for laminar conditions from Equation (7) are given versus the ice fraction at $-6\text{ }^{\circ}\text{C}$, with velocity of 0.3 m/s and tube diameter of 0.02 m . Differences

Table 1, Ice slurry data at $-6\text{ }^{\circ}\text{C}$ and 10 wt\% ice concentration

Substance	Initial concentration wt%	Viscosity $\text{mPa}\cdot\text{s}$	Apparent Cp $\text{kJ/kg}\cdot\text{K}$	Heat Transfer		Pressure drop kPa/m
				Turbulent $\text{W/m}^2\text{K}$	Laminar $\text{W/m}^2\text{K}$	
LiCl	5.28	3.92	41.08	8125	1009	6.98
NaCl	8.31	3.56	46.64	8481	1011	6.61
Methanol	8.22	4.47	48.28	6833	933	6.58
Ethanol	11.59	7.53	46.10	5098	891	7.48
Ethylene glycol	14.55	5.07	42.92	6305	908	6.97
Propylene glycol	15.49	6.96	41.76	5256	882	7.52
Potassium formate	10.63	3.61	48.02	8410	998	6.62

between freezing point depressants are small, but lithium chloride, sodium chloride and potassium formate have slightly higher heat transfer rates.

In Figure 5 pressure drop of ice slurries flowing through circular tubes at $-6\text{ }^{\circ}\text{C}$ is given. Ice fraction is the important factor, but difference between freezing point depressants can be up to 15%. Methanol, sodium chloride and potassium formate have lowest pressure drops.

In Table 2 the ice slurry data are displayed at $-24\text{ }^{\circ}\text{C}$ for 10 wt% ice, required for freezing applications. Lithium chloride compared to sodium chloride is more efficient at this temperature level. The apparent heat capacity at lower temperatures is lower and therefore relatively less important compared to the other parameters. From both Tables 1 and 2 it is observed that three substances have high heat storage capacity, high heat transfer and low viscosities and pressure drop. These are sodium chloride, lithium chloride and potassium formate.

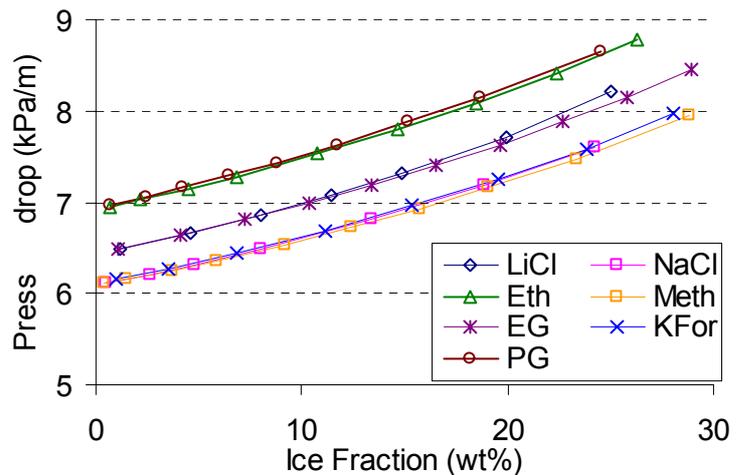


Figure 5, Pressure drop at $T = -6\text{ }^{\circ}\text{C}$, $v = 3\text{ m/s}$ and $D = 0.02\text{ m}$.

Table 2, Ice slurry data at $-24\text{ }^{\circ}\text{C}$ and 10 wt% ice concentration

Substance	Initial concentration wt%	Viscosity mPa.s	Apparent Cp kJ/kg.K	Heat Transfer		Pressure drop kPa/m
				Turbulent W/m^2K	Laminar W/m^2K	
LiCl	13.74	11.90	11.26	3378	808	10.20
NaCl	22.49	13.00	9.88	2957	788	9.93
Methanol	25.80	15.09	12.99	2170	646	8.82
Ethanol	30.46	46.45	13.68	1225	602	11.15
Ethylene glycol	36.08	27.24	10.21	1613	624	10.93
Propylene glycol	38.79	122.46	9.87	743	583	29.39
Potassium formate	29.09	9.80	10.39	3334	762	9.28

6. OTHER ADDITIVES

The use of antifreeze proteins that have a thermal hysteresis effect has been proposed to depress the freezing point. In cooling applications this is not advantageous because the freezing point is depressed, but the melting point of the ice remains equal. The substances therefore introduce an extra temperature difference in the secondary cooling cycle which needs to be overcome. This directly reduces energy efficiency of ice slurries in the secondary cooling cycle.

As property enhancement however, the proteins can be applied for various reasons: To control size and shape of ice crystals and improve ice slurry properties and also prevent recrystallisation in storage vessels. To reduce the supercooling required for nucleation of ice crystals, which can improve performance of ice slurry generators. The hysteresis needs to be as small as possible.

Some other properties of the additives have not been considered, for example corrosivity and toxicity. If a more corrosive substance depresses the freezing point with a smaller amount of additive required, the resulting ice slurry might be less corrosive. Also effects of anti-corrosion additives and surfactants on the freezing point depression have not been considered.

7. CONCLUSION

The molecular weight of a freezing point depressing substance gives a good indication of the efficiency of an ice slurry in a secondary cooling system when compared to similar substances with higher molecular weight. It is however not decisive under all conditions. In the three pairs of freezing point depressants that were compared for thermophysical properties, heat transfer and pressure drop, the effects were stronger at low temperatures. This is explained with the influence of the apparent heat capacity, which is relatively less important at low temperatures.

Molecules with low molecular weight tend to be more efficient for ice slurries, because the thermophysical properties of the ice slurries decrease when more solute is added, and additives of low molecular weight require low mass fractions added to depress the freezing point. From this research it followed that lithium chloride, sodium chloride and potassium formate are advantageous freezing point depressants.

8. REFERENCES

- Bel, O., Lallemand, A., Etude d'un fluide frigoporteur diphasique . International Journal of Refrigeration 1999 vol 22: p.164-187.
- Ben Lakhdar, M.A. Comportement thermo-hydraulique d'un fluide frigoporteur diphasique:Le coulis de glace, Thesis de l'INSA de Lyon, France 1998
- CRC Handbook of Chemistry and Physics, 78th edition 1997-1998, CRC Press Boca Raton NY.
- Frei, B., Egolf, P.W., Viscometry applied to the Bingham substance ice slurry, Proc. of the 2nd workshop on Ice Slurries, IIR Paris 2000, p 48-60.
- Grandum, S., Nakagomi, K., Characteristics of Ice Slurry Containing Antifreeze Protein for Ice Storage Applications, Journal of Thermophysics and Heat Transfer, vol.11 no.3, 1997, p 461-466
- Guilpart, J., Fournaison, L., Ben Lakhdar, M.A., Flick, D., Lallemand, A., Experimental study and calculation method of transport characteristics of ice slurries, 1st workshop on ice slurries of the IIR, Yverdon-les-Bains, Switzerland, IIF/IIR 1999 p74-82
- Kauffeld, M., Christensen, K.G., Lund, S., Hansen, T.M., Experience with Ice Slurry, Proc. of the 1st workshop on Ice Slurries, Yverdon-les-Bains, Switzerland, 1999, IIR. p42-73
- Knodel, B.D., France, D.M., Choi, U.S., Wambsganss, M.W., Heat transfer and pressure drop in ice-water slurries, Applied Thermal Engineering, vol. 20, 2000, p671-685
- Meewisse, J.W., Infante Ferreira, C.A., Comparing Alternative Ice Slurry Production Methods, Proc. of 20th International Congress of Refrigeration Sydney, IIR 1999, paper 580
- Meewisse, J.W., Infante Ferreira, C.A., Optimal Properties of Ice Slurries in Secondary Cooling Systems, Proc. of 4th IIR-Gustav Lorentzen Conference on natural working fluids at Purdue, Indiana USA, 2000, Editors Groll, Robinson, p513-520
- Melinder, A., Thermophysical properties of liquid secondary refrigerants, Handbook no. 12 of the Swedish Society of Refrigeration, 1997, Stockholm
- Soehnel, O., Densities of aqueous solutions of inorganic substances, Physical Sciences Data 22, Elsevier 1985
- Tareef *cited in*: Perry, R.H., Chilton, C.H., Chemical Engineers Handbook, 5th ed. NY, McGraw Hill, 1973
- Zakeri, G. R., 1997, Vacuum freeze refrigerated circuit (VFRC), a new system design for energy effective heat pumping systems, *Proc. Linz (Austria) Conf*, IIF/IIR, comm. E1,E2,B2: p. 182-190.