



Prediction of the freezing point of multicomponent liquid refrigerant solutions

Héctor A. Tello Alonso, Juan M. Peralta, Amelia C. Rubiolo, Susana E. Zorrilla*

Instituto de Desarrollo Tecnológico para la Industria Química (Universidad Nacional del Litoral, CONICET), Güemes 3450, S3000GLN, Santa Fe, Argentina

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ABSTRACT

The freezing point is one of the most critical properties required to complete the mathematical formulation related to the transport phenomena involved in the immersion chilling and freezing (ICF) of foods. Unfortunately, data for ternary and higher order systems are scarce. The aim of this work was to verify the validity of an excess Gibbs energy model for predicting the freezing point of multicomponent mixtures of electrolytes and non-electrolytes, considering the processing conditions used in immersion chilling and freezing of foods. The extended UNIQUAC model was used. Data obtained from literature corresponding to freezing points of the ternary systems: NaCl–KCl–H₂O, NaCl–CaCl₂–H₂O, NaCl–MgCl₂–H₂O and NaCl–EtOH–H₂O, were compared with predicted values. The model accuracy was satisfactory, the highest absolute deviation being smaller than 1.71 °C for the 378 data compared.

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1. Introduction

Immersion chilling and freezing (ICF) consist of soaking foods in a low freezing point liquid medium maintained at a low temperature. A number of economical and technical advantages over the conventional food chilling and freezing methods have been reported for the application of these refrigerating media: (1) high heat transfer rates with small temperature gradients, (2) fine ice crystal structure in foods is ensured, (3) the product surface freezes immediately in a solid crust that limits the osmotic transfer and gives an excellent appearance, (4) the operation is easy to maintain, convenient for automation and the labor costs are substantially reduced, and (5) the technology is environmentally friendly (Fikiin and Fikiin, 1998; Fikiin, 2003). Industrially, the ICF process has been used extensively for chilling or freezing fish (shrimp, crab, sardines, tuna, etc.) in brine (sodium chloride or even calcium chloride). Various products and processing conditions for binary and ternary aqueous solutions can be found in the literature. For example, diced carrots, sweet corn, beans and peas were frozen in a NaCl–glucose–H₂O solution; and haddock, salmon and tuna were frozen in a NaCl–CaCl₂–KCl–H₂O solution (Lucas and Raoult-Wack, 1998).

The freezing point of the refrigerating solution is a very important property not only because it is a critical value to complete the mathematical formulation of the transport phenomena involved but also because it allows predicting the thermophysical properties of the occluded solution in the food when a phase change exists (Zorrilla and Rubiolo, 2005a,b). The experimental or theoretical values of the freezing point of refrigerating solutions are scarce,

particularly for multicomponent systems. Ge and Wang (2009) predicted the values of freezing point for electrolyte solutions at different concentrations using the Pitzer theory. The model proposed was very simple but it is not suitable for solutions with very high concentrations. Haghghi et al. (2008) developed a semi-empirical model based on the cubic-plus-association equation of state and a Debye–Hückel electrostatic term was used to model long-range interactions in the electrolyte solutions. In the model, a water–salt interaction coefficient was defined. Although the predictions were good, the coefficients were only available for eight electrolyte solutions.

The thermodynamics-based models allow a convenient and flexible analysis of different physical scenarios (i.e. process simulation and optimization for a wide range of physical conditions to achieve the best possible operational conditions). Peralta et al. (2007) presented a thermodynamic model of excess Gibbs energy for predicting heat capacity, density and freezing point of liquid refrigerants used in ICF process. The model was checked for binary aqueous systems commonly used in chilling and freezing of foods. The objective of this work was to verify the validity of an excess Gibbs energy model for predicting the freezing point of multicomponent mixtures of electrolytes and non-electrolytes, considering the processing conditions used in immersion chilling and freezing of foods.

2. Theory

A modified version of the extended UNIQUAC model (Nicolaisen et al., 1993; Thomsen, 1997) developed by Sander et al. (1986), studied by Thomsen and co-workers, and proposed for the prediction of freezing point of multicomponent solutions (Peralta et al., 2007), was used. In this model, it is considered that the excess

* Corresponding author. Tel.: +54 342 451 1595; fax: +54 342 451 1079.
E-mail address: zorrilla@intec.unl.edu.ar (S.E. Zorrilla).

Nomenclature

A	Debye–Hückel parameter
a_w	water activity
b	constant, $47.4342 \text{ kg}^{1/2} \text{ kmol}^{-1/2}$
G	molar Gibbs energy, J kmol^{-1}
I	ionic strength, kmol kg^{-1}
M	molecular weight, kg kmol^{-1}
m	molality, kmol kg^{-1}
n	total mole number
P	pressure, Pa
q	surface area parameter of the UNIQUAC model
R	gas constant, $8314.47 \text{ J kmol}^{-1} \text{ K}^{-1}$
r	volume parameter of the UNIQUAC model
T	temperature, K
T_f	freezing point, K
u	binary interaction parameter of the UNIQUAC model (K)
u^o	parameter of Eq. (7), K
u^f	parameter of Eq. (7)
w	mass fraction, kg kg^{-1}
X	weight ratio
x	mole fraction considering the species dissociated, kmol kmol^{-1}
z	coordination number, $z = 10$
z_i	charge of ion i

Greek letters

γ activity coefficient

$\Delta \bar{G}_{fus}$	molar Gibbs energy of fusion of water, J kmol^{-1}
$\Delta \bar{H}_{fus}$	molar enthalpy of fusion of water, J kmol^{-1}
θ	surface area fraction defined in Eq. (3)
λ	parameter of Eq. (19)
μ	chemical potential, J kmol^{-1}
τ	UNIQUAC parameter defined in Eq. (6)
ϕ	volume fraction defined in Eq. (4)

Superscripts

<i>calc</i>	calculated
<i>exp</i>	experimental
<i>Liq</i>	liquid state
<i>o</i>	pure species
<i>Sol</i>	solid state

Subscripts

<i>C</i>	combinatorial
<i>D–H</i>	Debye–Hückel
<i>E</i>	excess
<i>i, j, k</i>	species i, j, k
<i>R</i>	residual
<i>s</i>	solvent
<i>w</i>	water

Gibbs energy consists of three contributions: combinatorial (G_C), residual (G_R) and Debye–Hückel (G_{D-H}).

$$G_E = G_C + G_R + G_{D-H} \quad (1)$$

The combinatorial term accounts for molecular size and shape differences, the residual term accounts for the molecular interactions, and the Debye–Hückel term accounts for the long-range electrostatic interactions. Each contribution was considered by the following expressions:

• Combinatorial term

$$\frac{G_C}{RT} = \sum_{i=1}^n x_i \ln \left(\frac{\phi_i}{x_i} \right) - \frac{z}{2} \sum_{i=1}^n q_i x_i \ln \left(\frac{\phi_i}{\theta_i} \right) \quad (2)$$

$$\theta_i = \frac{x_i q_i}{\sum_{j=1}^n x_j q_j} \quad (3)$$

$$\phi_i = \frac{x_i r_i}{\sum_{j=1}^n x_j r_j} \quad (4)$$

• Residual term

$$\frac{G_R}{RT} = - \sum_{i=1}^n q_i x_i \ln \left(\sum_{j=1}^n \theta_j \tau_{ji} \right) \quad (5)$$

$$\tau_{ji} = \exp \left[\frac{-(u_{ji} - u_{ii})}{T} \right] \quad (6)$$

$$u_{ji} = u_{ji}^o + u_{ji}^f (T - 298.15) \quad (7)$$

• Debye–Hückel term

$$\frac{G_{D-H}}{RT} = -x_s M_s \frac{4A}{b^3} \left[\ln (1 + bI^{1/2}) - bI^{1/2} + \frac{b^2 I}{2} \right] \quad (8)$$

$$I = \frac{1}{2} \sum_{i=1}^n m_i z_i^2 \quad (9)$$

The freezing point of a pure solvent is the temperature at which solid and liquid phases can exist in equilibrium. In the case of aqueous solutions, the addition of a solute lowers the freezing point and enables the liquid and solid phases of the system to exist in equilibrium at various temperatures (Fennema et al., 1973). At equilibrium, the chemical potential of water must be the same in both phases.

$$\mu_w^{Sol} = \mu_w^{Liq} \quad (10)$$

Moreover, considering water as a pure substance in the solid phase (pure ice) and as a species in the liquid phase, results:

$$\mu_w^{Sol,o} = \mu_w^{Liq,o} + RT \ln a_w \quad (11)$$

Rearranging Eq. (11) leads to

$$\mu_w^{Liq,o} - \mu_w^{Sol,o} = \Delta \bar{G}_{fus} = -RT \ln a_w \quad (12)$$

Taking into account the Gibbs–Helmholtz equation:

$$\left. \frac{\partial \left(\frac{\Delta \bar{G}}{T} \right)}{\partial T} \right|_P = - \frac{\Delta \bar{H}}{T^2} \quad (13)$$

Eq. (12) becomes

$$R \ln a_w = \int_{T_o}^{T_f} \frac{\Delta \bar{H}_{fus}}{T^2} dT \quad (14)$$

Taking into account that:

$$\ln a_w = \left. \frac{\partial \left(\frac{nG_E}{RT} \right)}{\partial n_w} \right|_{P,T} + \ln x_w \quad (15)$$

and using Eqs. (1)–(9), the expression for $\ln a_w$ is (Peralta et al., 2007):

$$\ln a_w = \ln \left(\frac{\phi_w}{x_w} \right) + \frac{z}{2} q_w \ln \left(\frac{\theta_w}{\phi_w} \right) + \left[\frac{z}{2} (r_w - q_w) - (r_w - 1) \right] - \frac{\phi_w}{x_w} \left(\sum_{i=1}^n x_i l_i \right) + q_w \left[1 - \ln \left(\sum_{i=1}^n \theta_i \tau_{iw} \right) - \sum_{i=1}^n \frac{\theta_i \tau_{wi}}{\sum_{j=1}^n \theta_j \tau_{ji}} \right] + \frac{2AM_w}{b^3} \left[\left(1 + bl^{\frac{1}{2}} \right) - \frac{1}{\left(1 + bl^{\frac{1}{2}} \right)} - 2 \ln \left(1 + bl^{\frac{1}{2}} \right) \right] + \ln x_w \tag{16}$$

where

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \tag{17}$$

Table 1
Characteristics of the experimental data for the system NaCl–KCl–H₂O (Hall et al., 1988). $X = w_{NaCl}/(w_{NaCl} + w_{KCl})$.

X	w _{NaCl} (kg kg ⁻¹)	w _{KCl} (kg kg ⁻¹)	T _f (°C)
0	0	0–0.1955	0 to –10.69
0.2	0–0.0392	0–0.1566	0 to –11.50
0.4	0–0.0851	0–0.1277	0 to –14.00
0.6	0–0.1367	0–0.0912	0 to –17.00
0.8	0–0.1958	0–0.0489	0 to –21.00
1	0–0.2320	0	0 to –21.21

Table 2
Characteristics of the experimental data for the system NaCl–CaCl₂–H₂O (Oakes et al., 1990). $X = w_{NaCl}/(w_{NaCl} + w_{CaCl_2})$.

X	w _{NaCl} (kg kg ⁻¹)	w _{CaCl₂} (kg kg ⁻¹)	T _f (°C)
0	0	0–0.3059	0 to –51.20
0.169	0.0353–0.0452	0.1733–0.2223	–19.99 to –34.03
0.195	0–0.0428	0–0.1766	0 to –22.01
0.393	0–0.0971	0–0.1499	0 to –26.93
0.593	0–0.1389	0–0.0954	0 to –23.28
0.796	0–0.1881	0–0.0482	0 to –22.48
1	0–0.2334	0	0 to –21.48

Table 3
Characteristics of the experimental data for the system NaCl–MgCl₂–H₂O. $X = w_{NaCl}/(w_{NaCl} + w_{MgCl_2})$.

X	w _{NaCl} (kg kg ⁻¹)	w _{MgCl₂} (kg kg ⁻¹)	T _f (°C)	Source
0	0	0–0.1618	0 to –18.394	Gibbard and Gossmann (1974)
0	0	0–0.15	0 to –15.58	Haghighi et al. (2008)
0	0	0.111–0.2060	–10 to –33.6	Seidell (1940)
0	0	0.2098	–33.6	Spencer et al. (1990)
0.3	0.0147–0.0380	0.0340–0.0875	–2.85 to –10.65	Dubois and Marignac (1997)
0.380	0–0.0459	0–0.0748	0 to –9.666	Gibbard and Gossmann (1974)
0.5	0.0221–0.0572	0.0222–0.0574	–2.55 to –8.72	Dubois and Marignac (1997)
0.686	0–0.0771	0–0.0353	0 to –8.111	Gibbard and Gossmann (1974)
0.847	0–0.1066	0–0.0192	0 to –9.09	Gibbard and Gossmann (1974)
1	0–0.2334	0	0 to –21.48	Oakes et al. (1990)

Table 4
Characteristics of the experimental data for the system NaCl–EtOH–H₂O. $X = w_{NaCl}/(w_{NaCl} + w_{EtOH})$.

X	w _{NaCl} (kg kg ⁻¹)	w _{EtOH} (kg kg ⁻¹)	T _f (°C)	Source
0	0	0–0.05	0 to –1.941	Weast (1974)
0	0	0.0114–0.0225	–0.456 to –0.907	Desnoyers et al. (1976)
0.389	0.0072–0.0141	0.0113–0.0222	–0.899 to –1.813	Desnoyers et al. (1976)
1	0–0.05	0	0 to –2.984	Weast (1974)
1	0.0072–0.0144	0	0.423 to –0.837	Desnoyers et al. (1976)

Finally, if the functionality of $\Delta\bar{H}_{fus}$ with temperature is known (Dougherty and Howard, 1998) and Eq. (14) is integrated, the freezing point of the solution (T_f) can be calculated.

3. Materials and methods

To verify the validity of the model, experimental data obtained from the literature were compared with the predicted values. Experimental freezing point values of the ternary systems NaCl–KCl–H₂O (Hall et al., 1988), NaCl–CaCl₂–H₂O (Oakes et al., 1990), NaCl–MgCl₂–H₂O (Seidell, 1940; Gibbard and Gossmann, 1974; Spencer et al., 1990; Dubois and Marignac, 1997; Haghighi et al., 2008) and NaCl–EtOH–H₂O (Weast, 1974; Desnoyers et al., 1976) were used. It is worth mentioning that these ternary solutions have great potentiality to be used in the ICF processes. The experimental freezing point values of ternary solutions are generally shown as function of a weight ratio X. This ratio is defined as $X = w_{NaCl}/(w_{NaCl} + w_i)$, where i is CaCl₂, KCl, MgCl₂ or EtOH. For example, in the system NaCl–KCl–H₂O, $X = w_{NaCl}/(w_{NaCl} + w_{KCl})$. For the systems NaCl–KCl–H₂O, NaCl–CaCl₂–H₂O, NaCl–MgCl₂–H₂O, and NaCl–EtOH–H₂O, 101, 174, 72, and 31 experimental data were found, respectively (Tables 1–4). Hall et al. (1988) and Oakes et al. (1990) reported a precision of the temperature measurements generally better than ±0.05 °C, while Gibbard and Gossmann (1974) and Desnoyers et al. (1976) reported uncertainties of ±0.001 °C in the experimental freezing points.

3.1. UNIQUAC model parameters

The extended UNIQUAC parameters for the study cases were obtained from Thomsen et al. (1996), Christensen and Thomsen (2003), García et al. (2005) and García et al. (2006) (Tables 5–7).

The Debye–Hückel parameter as proposed by Nicolaisen et al. (1993) was used.

$$A = 35.765 + 4.222 \times 10^{-2} (T - 273.15) + 3.681 \times 10^{-4} (T - 273.15)^2 \tag{18}$$

The expression used for the $\Delta\bar{H}_{fus}$ is (Rahman, 2009):

$$\Delta\bar{H}_{fus} = \lambda_1 + \lambda_2 T + \lambda_3 T^2 \tag{19}$$

where $\lambda_1 = -9700667.93 \text{ J kmol}^{-1}$, $\lambda_2 = 78167.031 \text{ J kmol}^{-1} \text{ K}^{-1}$, and $\lambda_3 = -75.49542 \text{ J kmol}^{-1} \text{ K}^{-2}$.

Finally, water was used as the solvent for all the cases studied.

Table 5
UNIQUAC q and r parameters (Thomsen et al., 1996; García et al., 2005, 2006).

Species	q	r
H ₂ O	1.400	0.9200
EtOH	5.880	5.880
Na ⁺	1.1990	1.4034
K ⁺	2.4306	2.2304
Ca ⁺²	1.480	3.870
Mg ⁺²	5.410	2.540
Cl ⁻	10.197	10.386

Table 6
UNIQUAC interaction parameters u_{ij}^0 (Christensen and Thomsen, 2003; García et al., 2005, 2006).

ij	H ₂ O	EtOH	Na ⁺	K ⁺	Ca ⁺²	Mg ⁺²	Cl ⁻
H ₂ O	0	496.8	733.286	535.023	496.352	-2.0428	1523.39
EtOH		624.0	2795.0				1650.0
Na ⁺			0	-46.194	-100.03	-70.956	1443.23
K ⁺				0	-402.95		1465.18
Ca ⁺²					0		1805.6
Mg ⁺²						0	2049
Cl ⁻							2214.81

Table 7
UNIQUAC interaction parameters u_{ij}^t (Christensen and Thomsen, 2003; García et al., 2005, 2006).

ij	H ₂ O	EtOH	Na ⁺	K ⁺	Ca ⁺²	Mg ⁺²	Cl ⁻
H ₂ O	0	0.282	0.48719	0.99356	-8.0654	-3.5542	14.631
EtOH		0	0				14.32
Na ⁺			0	0.11899	-4.6556	1.3394	15.635
K ⁺				0	-3.3100		15.329
Ca ⁺²					0		11.14
Mg ⁺²						0	12.132
Cl ⁻							14.436

4. Results and discussion

In Figs. 1–4, the predicted freezing point values are compared with the experimental ones for the systems of NaCl–KCl–H₂O, NaCl–CaCl₂–H₂O, NaCl–MgCl₂–H₂O, and NaCl–EtOH–H₂O, respectively. A satisfactory accuracy can be observed.

In Figs. 5–8, the comparison of the theoretical values with the experimental ones is shown. The highest absolute difference between the theoretical and experimental values was 0.61 °C for the NaCl–KCl–H₂O system, 0.82 °C for the NaCl–CaCl₂–H₂O system, 1.71 °C for the NaCl–MgCl₂–H₂O system, and 0.15 °C for the NaCl–EtOH–H₂O system. It is worth mentioning that the highest difference between the theoretical and experimental values for the NaCl–MgCl₂–H₂O system is related to the uncertainty of the experimental determinations close to the eutectic temperature (Seidell, 1940; Spencer et al., 1990).

The prediction of the freezing point is very accurate. The errors observed may be explained taking into account the nature of the solutes. In the case of electrolytes, the ionic radii and the hydration may affect the contributions considered in the thermodynamic model (Zuend et al., 2008). The hydration effect is important at low electrolyte concentration, the effect being more important for smaller ionic radii and for higher ion-charge. For example, the ion Ca⁺² is smaller and it has a higher charge than K⁺, therefore the hydration effect would be more important in the system with CaCl₂ than in the system with KCl. Other source of error may be related to the fact that the UNIQUAC parameters used were obtained for a temperature range above 0 °C and therefore, higher

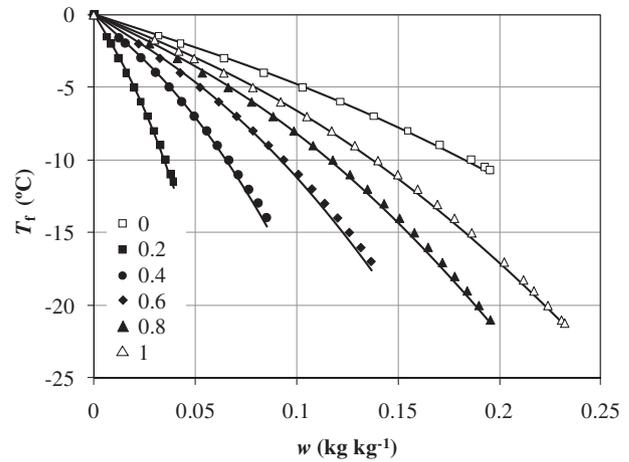


Fig. 1. Freezing point for the system NaCl–KCl–H₂O for different values of X . For $X = 0$, w corresponds to the mass fraction of KCl. For $X \neq 0$, w corresponds to the mass fraction of NaCl. Symbols correspond to experimental data and lines to calculated values. Source: (All symbols) Hall et al. (1988).

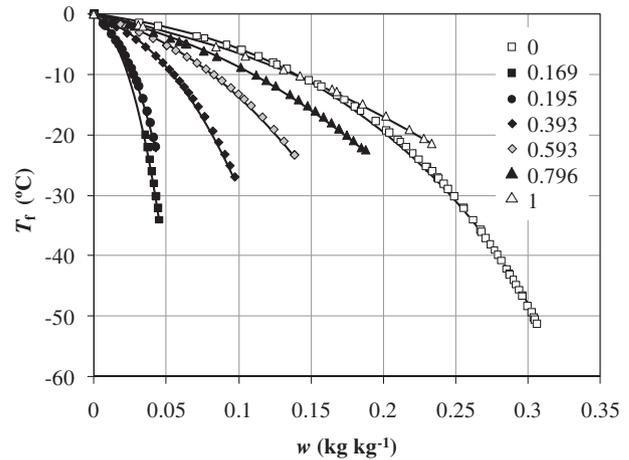


Fig. 2. Freezing point for the system NaCl–CaCl₂–H₂O for different values of X . For $X \neq 0$, w corresponds to the mass fraction of CaCl₂. Symbols correspond to experimental data and lines to calculated values. Source: (All symbols) Oakes et al. (1990).

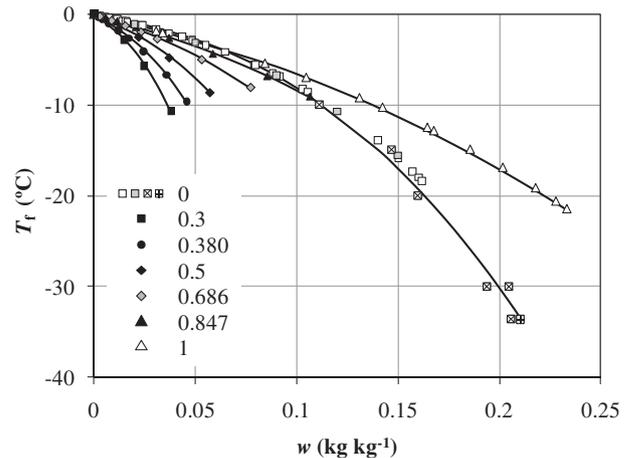


Fig. 3. Freezing point for the system NaCl–MgCl₂–H₂O for different values of X . For $X = 0$, w corresponds to the mass fraction of MgCl₂. For $X \neq 0$, w corresponds to the mass fraction of NaCl. Sources: (⊠) Seidell (1940), (□, ●, ◆, ▲) Gibbard and Gossmann (1974), (△) Oakes et al. (1990), (⊞) Spencer et al. (1990), (■, ◆) Dubois and Marignac (1997), (◻) Haghighi et al. (2008).

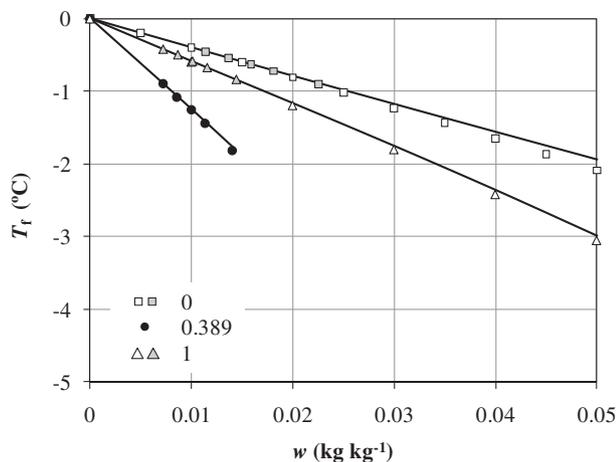


Fig. 4. Freezing point for the system NaCl–EtOH–H₂O for different values of X. For X = 0, w corresponds to the mass fraction of EtOH. For X ≠ 0, w corresponds to the mass fraction of NaCl. Symbols correspond to experimental data and lines to calculated values. Sources: (□, △) Weast (1974), (■, ●, ▲) Desnoyers et al. (1976).

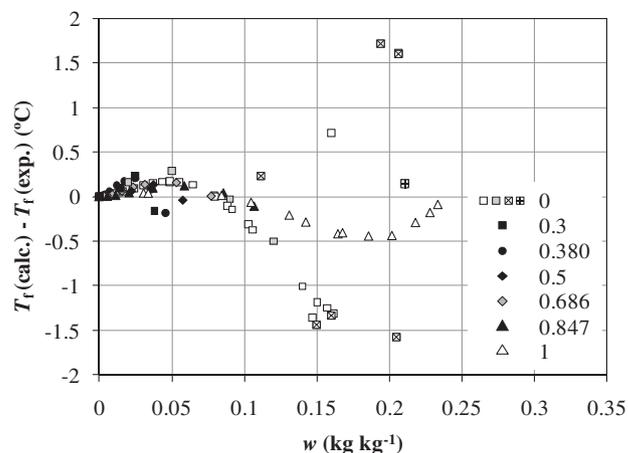


Fig. 7. Comparison of experimental and theoretical data for the system NaCl–MgCl₂–H₂O for different values of X. For X = 0, w corresponds to the mass fraction of MgCl₂. For X ≠ 0, w corresponds to the mass fraction of NaCl. Sources: (⊠) Seidell (1940), (□, ●, ◆, ▲) Gibbard and Gossmann (1974), (△) Oakes et al. (1990), (⊞) Spencer et al. (1990), (■, ◆) Dubois and Marignac (1997), (◻) Haghighi et al. (2008).

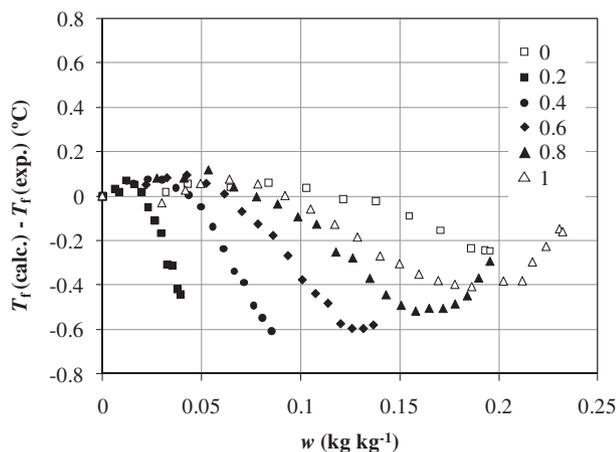


Fig. 5. Comparison of experimental and theoretical data for the system NaCl–KCl–H₂O for different values of X. For X = 0, w corresponds to the mass fraction of KCl. For X ≠ 0, w corresponds to the mass fraction of NaCl. Source: (All symbols) Hall et al. (1988).

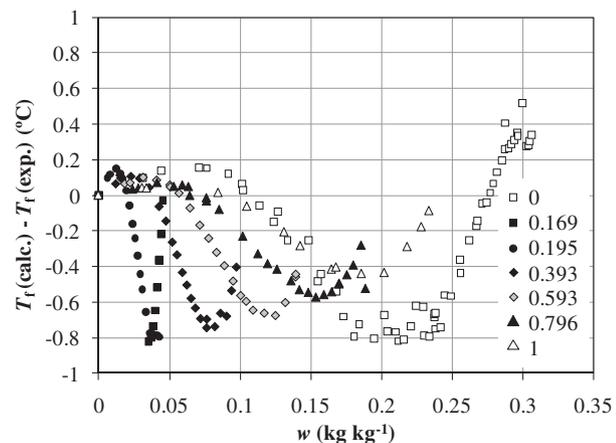


Fig. 6. Comparison of experimental and theoretical data for the system NaCl–CaCl₂–H₂O for different values of X. For X = 0, w corresponds to the mass fraction of CaCl₂. For X ≠ 0, w corresponds to the mass fraction of NaCl. Source: (All symbols) Oakes et al. (1990).

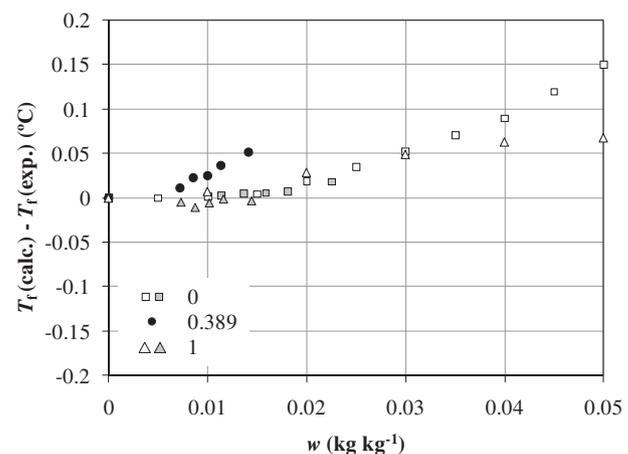


Fig. 8. Comparison of experimental and theoretical data for the system NaCl–EtOH–H₂O for different values of X. For X = 0, w corresponds to the mass fraction of EtOH. For X ≠ 0, w corresponds to the mass fraction of NaCl. Sources: (□, △) Weast (1974), (■, ●, ▲) Desnoyers et al. (1976).

extrapolation errors may be expected in the temperature range of liquid refrigerants.

Although there are practically unlimited possibilities to combine constituents and to formulate appropriate multicomponent solutions, there are scarce data related to their freezing points. Therefore, this work may contribute with a useful tool for the prediction of freezing point of multicomponent liquid refrigerants.

5. Conclusions

The extended UNIQUAC model was adequate for predicting the freezing point in multicomponent systems related to the cooling and/or freezing by immersion. A satisfactory accuracy was observed for the systems studied. The model may be used to explore different scenarios where at present there is a lack of experimental and theoretical data.

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