

Prediction of heat capacity, density and freezing point of liquid refrigerant solutions using an excess Gibbs energy model

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Abstract

Immersion chilling and freezing (ICF) of foods use aqueous solutions at low temperature that are considered secondary refrigerants. These solutions contain solutes such as NaCl, CaCl₂, KCl, ethanol, glucose, etc. The ICF processes have several advantages over the conventional food chilling and freezing methods. The aim of this work was to study the behavior of an excess Gibbs energy model for predicting thermodynamic properties of mixtures of electrolytes and non-electrolytes, considering the physical conditions used in immersion chilling and freezing of foods. The extended UNIQUAC model was used. Data obtained from literature for heat capacity, density and freezing point for binary aqueous solutions of NaCl, CaCl₂, KCl and ethanol were compared with predicted values. Additional parameters for the density estimation were included into the model. In general, the model accuracy was satisfactory.

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1. Introduction

Immersion chilling and freezing processes (ICF) and a recently developed method of freezing called hydrofluidization (Fikiin & Fikiin, 1998) use liquid solutions at low temperature. Generally, those solutions are aqueous solutions of solutes such as NaCl, CaCl₂, KCl, ethanol, glucose, etc. (Lucas & Raoult-Wack, 1998). 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, 2003; Fikiin & Fikiin, 1998).

Mathematical models for predicting heat and mass transfer in ICF processes have been published recently in the literature (Lucas, Chourot, Bohuon, & Flick, 2001; Zorrilla & Rubiolo, 2005a, 2005b). In those models, foods are considered as heterogeneous systems composed by three phases: ice, aqueous solution and solid food. Those models take into account the heat and mass transfer that occurs among the three phases. For each phase, thermophysical properties are necessary to complete the mathematical description (i.e. to study the food freezing, it is very important to have information about the thermophysical properties of the aqueous solution occluded in the food). On the other hand, the transport properties at the food surface (i.e. heat and mass transfer coefficients) are commonly determined from the thermophysical properties of the liquid refrigerant (Kondjoyan, 2006). Moreover, besides the food industry, thermophysical properties of aqueous refrigerants at temperatures below 0 °C have important geochemical and geophysical implications in

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Nomenclature

A	Debye–Hückel parameter defined in Eq. (11)	<i>Greek letters</i>	
a_w	water activity	β	expansion coefficient of solvent, Pa ⁻¹
b	constant, 47.4342 kg ^{1/2} kmol ^{-1/2}	γ	activity coefficient
C_p	molar heat capacity, J kmol ⁻¹ K ⁻¹	$\Delta\bar{G}_{\text{fus}}$	molar Gibbs energy of fusion of water, J kmol ⁻¹
\bar{C}_p	partial molar heat capacity, J kmol ⁻¹ K ⁻¹	$\Delta\bar{H}_{\text{fus}}$	molar enthalpy of fusion of water, J kmol ⁻¹
F	Faraday constant, 9.65×10^7 C kmol ⁻¹	$\delta_{1,i} - \delta_{7,i}$	parameters of Eqs. (45), (48) and (49)
G	molar Gibbs energy, J kmol ⁻¹	ϵ_o	vacuum permittivity, 8.8541×10^{-12} C ² J ⁻¹ m ⁻¹
I	ionic strength, kmol kg ⁻¹	ϵ_r	dielectric constant
M	molecular weight, kg kmol ⁻¹	θ	surface area fraction defined in Eq. (4)
MPE	mean percent error	λ	parameter of Eq. (50)
m	molality, kmol kg ⁻¹	μ	chemical potential, J kmol ⁻¹
N	number of data	ρ	density, kg m ⁻³
n	total mole number	τ	UNIQUAC parameter defined in Eq. (7)
N_A	Avogadro's number, 6.023×10^{26} particles kmol ⁻¹	ϕ	volume fraction defined in Eq. (5)
OF	objective function defined in Eq. (46)	<i>Superscripts</i>	
P	pressure, Pa	∞	infinite dilution, $x_s \rightarrow 1$
q	surface area parameter of the UNIQUAC model	calc	calculated
R	gas constant, 8314.47 J kmol ⁻¹ K ⁻¹	exp	experimental
r	volume parameter of the UNIQUAC model	IDS	ideal dilute solution
T	temperature, K	Liq	liquid state
u	binary interaction parameter of the UNIQUAC model, K	o	pure species
u^o	parameter of Eq. (8), K	P	first derivative with respect to pressure
u^t	parameter of Eq. (8)	PS	perfect solution
V	molar volume, m ³ kmol ⁻¹	Sol	solid state
\bar{V}	partial molar volume, m ³ kmol ⁻¹	<i>Subscripts</i>	
w	mass fraction, kg kg ⁻¹	C	combinatorial
x	mole fraction considering the species dissociated, kmol kmol ⁻¹	D–H	Debye–Hückel
y	property	E	excess
z	coordination number, $z = 10$	i, j, k	species i, j, k
z_i	charge of ion i	R	residual
		s	solvent
		SS	standard state
		w	water

terrestrial, marine, and atmospheric environments in cold regions (Mironenko, Grant, & Marion, 1997).

As pointed out by Fikiin, Tsvetkov, Laptev, Fikiin, and Kolodyaznaya (2003) the available data for the physical properties and behavior of multicomponent refrigerating media used in ICF processes are still scarce. A number of experimental relationships for estimating thermodynamic properties of binary and ternary refrigerating media are available in the literature, mostly in a polynomial form (Fikiin et al., 2003; Lugo, Fournaison, Chourot, & Guilpart, 2002; Rahman, 1995); therefore, they have restrictions due to experimental validity range. Simultaneously, there is a need for theoretical approaches and thermodynamics-based models, which can permit 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).

The objective of this work was to study the behavior of an excess Gibbs energy model for predicting the thermodynamic properties of mixtures of electrolytes and non-electrolytes, considering temperature, pressure and concentration conditions used in immersion chilling and freezing of foods.

2. Theory

The molar excess Gibbs energy (G_E) for a system of n chemical species is:

$$G_E = \sum_{i=1}^n x_i RT \ln \gamma_i. \quad (1)$$

The extended UNIQUAC model proposed by Sander, Fredenslund, and Rasmussen (1986), modified by Nicolaisen, Rasmussen, and Sørensen (1993) and studied by Thomsen,

Rasmussen, and Gani (1996), Thomsen (1997), Iliuta, Thomsen, and Rasmussen (2000) Thomsen, Iliuta, and Rasmussen (2004), was selected to study the behavior of refrigerant solutions. It is considered that the excess Gibbs energy consists of three contributions: combinatorial (G_C), residual (G_R) and Debye–Hückel (G_{D-H}).

$$G_E = G_C + G_R + G_{D-H}. \quad (2)$$

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*

$$\frac{G_C}{RT} = \sum_{i=1}^n x_i \ln \left(\frac{\phi_i}{x_i} \right) - \frac{z}{2} \sum_{i=1}^n q_i x_i \ln \left(\frac{\phi_i}{\theta_i} \right), \quad (3)$$

$$\theta_i = \frac{x_i q_i}{\sum_{j=1}^n x_j q_j}, \quad (4)$$

$$\phi_i = \frac{x_i r_i}{\sum_{j=1}^n x_j r_j}. \quad (5)$$

- *Residual term*

$$\frac{G_R}{RT} = - \sum_{i=1}^n q_i x_i \ln \left(\sum_{j=1}^n \theta_j \tau_{ji} \right), \quad (6)$$

$$\tau_{ji} = \exp \left[\frac{-(u_{ji} - u_{ii})}{T} \right], \quad (7)$$

$$u_{ji} = u_{ji}^o + u_{ji}^t (T - 298.15). \quad (8)$$

- *Debye–Hückel term*

$$\frac{G_{D-H}}{RT} = -x_s M_s \frac{4A}{b^3} \left[\ln(1 + bI^{1/2}) - bI^{1/2} + \frac{b^2 I}{2} \right], \quad (9)$$

$$I = \frac{1}{2} \sum_{i=1}^n m_i z_i^2, \quad (10)$$

$$A = \frac{F^3}{4\pi N_A} \left[\frac{\rho_s}{2(\epsilon_o \epsilon_r RT)^3} \right]^{1/2}. \quad (11)$$

Taking into account the physical state of the pure species and their standard states, the activity coefficients are related by:

$$\ln \gamma_i^{(IDS)} = \ln \gamma_i^{(PS)} - \ln \gamma_i^\infty, \quad (12)$$

$$\ln \gamma_i^\infty = \lim_{x_s \rightarrow 1} (\ln \gamma_i^{(PS)}), \quad (13)$$

$\gamma_i^{(IDS)}$ and $\gamma_i^{(PS)}$ are the activity coefficients of the i th species when ideal dilute solution and perfect solution are the standard states, respectively. γ_i^∞ is the activity coefficient of the i th species at infinite dilution when perfect solution is the standard state.

Finally, using Eq. (1) and taking into account Eqs. (2) and (12), the equation for the molar excess Gibbs energy of the system is obtained:

$$\begin{aligned} \frac{G_E}{RT} = & \sum_{i=1}^l x_i \sum_{f=1}^3 \ln \gamma_{i,f}^{(PS)} + \sum_{i=l+1}^r x_i \sum_{f=1}^3 \left(\ln \gamma_{i,f}^{(PS)} - \ln \gamma_{i,f}^\infty \right) \\ & + \sum_{i=r+1}^n x_i \sum_{f=1}^2 \left(\ln \gamma_{i,f}^{(PS)} - \ln \gamma_{i,f}^\infty \right) + \sum_{i=r+1}^n x_i \ln \gamma_{i,D-H}^{(IDS)}, \end{aligned} \quad (14)$$

where the subscript f indicates the type of interaction ($f=1$ means combinatorial, $f=2$ means residual and $f=3$ means Debye–Hückel). The first term of Eq. (14) is related to molecular species that in their pure states are liquid (i.e. water, ethanol, etc.), the second term is related to molecular species that in their pure state are solids (i.e. sugars, urea, etc.) and the last two terms are related to ionic species (i.e. NaCl, KCl, etc.)

The activity coefficient for species i is obtained by:

$$\ln \gamma_i = \left. \frac{\partial (nG_E/RT)}{\partial n_i} \right|_{P,T,n_{j \neq i}}. \quad (15)$$

Therefore, the activity coefficients derived from the proposed model and used in Eq. (14) are:

$$\ln \gamma_{i,C}^{(PS)} = \ln \left(\frac{\phi_i}{x_i} \right) + \frac{z}{2} q_i \ln \left(\frac{\theta_i}{\phi_i} \right) + l_i - \frac{\phi_i}{x_i} \left(\sum_{j=1}^n x_j l_j \right), \quad (16)$$

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

$$\ln \gamma_{i,R}^{(PS)} = q_i \left[1 - \ln \left(\sum_{j=1}^n \theta_j \tau_{ji} \right) - \sum_{j=1}^n \frac{\theta_j \tau_{ij}}{\sum_{k=1}^n \theta_k \tau_{kj}} \right], \quad (18)$$

$$\ln \gamma_{i,D-H}^{(PS)} = \frac{2AM_s}{b^3} \left[(1 + bI^{1/2}) - \frac{1}{(1 + bI^{1/2})} - 2 \ln(1 + bI^{1/2}) \right], \quad (19)$$

$$\ln \gamma_{i,D-H}^{(IDS)} = -Az_i^2 \frac{I^{1/2}}{1 + bI^{1/2}}, \quad (20)$$

$$\ln \gamma_{i,C}^\infty = \ln \left(\frac{r_i}{r_s} \right) + \frac{z}{2} q_i \ln \left(\frac{q_i r_s}{q_s r_i} \right) + l_i - \frac{r_i}{r_s} l_i, \quad (21)$$

$$\ln \gamma_{i,R}^\infty = q_i [1 - \ln(\tau_{si}) - \tau_{is}], \quad (22)$$

$$\ln \gamma_{i,D-H}^\infty = 0. \quad (23)$$

The ionic strength is calculated by:

$$I = \frac{1}{2} \frac{\sum_{i=1}^n x_i z_i^2}{x_w M_w}, \quad (24)$$

where water is considered as the solvent.

In the model used in this work, molar fractions of the dissociated species must be used (i.e. for a solution of NaCl and H_2O , x_{Na^+} , x_{Cl^-} and x_{H_2O} were considered).

2.1. Heat capacity

The relationship between the molar Gibbs energy and the molar heat capacity of a system is:

$$Cp = -T \frac{\partial^2 G}{\partial T^2} \Big|_{P,x} \quad (25)$$

Using Eq. (14) in Eq. (25), the following equation is obtained:

$$Cp_E = -RT \left\{ \sum_{i=1}^l x_i \sum_{f=1}^3 \frac{\partial^2 (T \ln \gamma_{i,f}^{(PS)})}{\partial T^2} + \sum_{i=l+1}^r x_i \sum_{f=1}^3 \left(\frac{\partial^2 (T \ln \gamma_{i,f}^{(PS)})}{\partial T^2} - \frac{\partial^2 (T \ln \gamma_{i,f}^{\infty})}{\partial T^2} \right) + \sum_{i=r+1}^n x_i \sum_{f=1}^2 \left(\frac{\partial^2 (T \ln \gamma_{i,f}^{(PS)})}{\partial T^2} - \frac{\partial^2 (T \ln \gamma_{i,f}^{\infty})}{\partial T^2} \right) + \sum_{i=r+1}^n x_i \frac{\partial^2 (T \ln \gamma_{i,D-H}^{(IDS)})}{\partial T^2} \right\}. \quad (26)$$

Finally, the molar heat capacity of the system is calculated by:

$$Cp = Cp_E + Cp_{SS}, \quad (27)$$

where

$$Cp_{SS} = \sum_{i=1}^n x_i \bar{C}p_{i,SS}. \quad (28)$$

If the species i is solid in its pure state, $\bar{C}p_{i,SS} = \bar{C}p_i^{\infty}$ and if the species i is liquid in its pure state, $\bar{C}p_{i,SS} = Cp_i^o$.

2.2. Density

The density of a solution can be defined as follows:

$$\rho = \frac{M}{V} = \frac{1}{V} \sum_{i=1}^n x_i M_i. \quad (29)$$

The relationship between the molar Gibbs energy and the molar volume of the system is:

$$V = \frac{\partial G}{\partial P} \Big|_{T,x} \quad (30)$$

Using Eq. (14) in Eq. (30) results:

$$V_E = RT \left\{ \sum_{i=1}^l x_i \sum_{f=1}^3 \frac{\partial (\ln \gamma_{i,f}^{(PS)})}{\partial P} + \sum_{i=l+1}^r x_i \sum_{f=1}^3 \left[\frac{\partial (\ln \gamma_{i,f}^{(PS)})}{\partial P} - \frac{\partial (\ln \gamma_{i,f}^{\infty})}{\partial P} \right] + \sum_{i=r+1}^n x_i \sum_{f=1}^2 \left[\frac{\partial (\ln \gamma_{i,f}^{(PS)})}{\partial P} - \frac{\partial (\ln \gamma_{i,f}^{\infty})}{\partial P} \right] + \sum_{i=r+1}^n x_i \frac{\partial (\ln \gamma_{i,D-H}^{(IDS)})}{\partial P} \right\}. \quad (31)$$

In the excess Gibbs energy model used, the temperature influence is considered through the binary interaction parameters (Eqs. (7) and (8)). Some authors have considered pressure influence on G for predicting volumetric properties (Humffray, 1989; Sardroodi & Zafarani-Moattar, 2004; Wang, Anderko, & Young, 2002; Zafarani-Moattar & Sardroodi, 2003). In general, the authors considered additional interaction parameters and very good results were obtained for predicting the density of several aqueous electrolyte solutions at temperatures above 0 °C. On the other hand, although the parameters q and r theoretically are function only of the nature of the molecule or ion (Abrams & Prausnitz, 1975; Banerjee, Singh, Sahoo, & Khanna, 2005), some authors considered those parameters as function of temperature to achieve a better model accuracy (Kabadi, 1999; Wiśniewska-Gocłowska & Malanowski, 2001). Therefore, it was considered that q , r , and A (Eqs. (4), (5), (11)) depend on pressure. In this work, the parameters q and r depending on pressure are:

$$q_i = q_i^{\text{biblio}} + q_i^P (P - P_0), \quad (32)$$

$$r_i = r_i^{\text{biblio}} + r_i^P (P - P_0), \quad (33)$$

where q_i^{biblio} and r_i^{biblio} are the original parameters found in the bibliography and q_i^P and r_i^P are fitting parameters. Eqs. (32) and (33) were used because of their convenient mathematical form. Differentiating Eqs. (32) and (33) with respect to pressure and taking into account that ICF processes are carried out at constant atmospheric pressure P_0 , the values of q_i^P and r_i^P can be fitted using the density data. It should be pointed out that when Eqs. (32) and (33) are used in the parameter τ , $q_i = q_i^{\text{biblio}}$ and $r_i = r_i^{\text{biblio}}$.

Finally, the molar volume of the system is calculated by:

$$V = V_E + V_{SS}, \quad (34)$$

where

$$V_{SS} = \sum_{i=1}^n x_i \bar{V}_{i,SS}. \quad (35)$$

If the species i is solid in its pure state, $\bar{V}_{i,SS} = \bar{V}_i^{\infty}$ and if the species i is liquid in its pure state, $\bar{V}_{i,SS} = V_i^o$.

2.3. Freezing point

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, Powrie, & Marth, 1973). At equilibrium, the chemical potential of water must be the same in both phases

$$\mu_w^{\text{Sol}} = \mu_w^{\text{Liq}}. \quad (36)$$

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

$$\mu_w^{\text{Sol},o} = \mu_w^{\text{Liq},o} + RT \ln a_w. \quad (37)$$

Rearranged Eq. (37) leads to

$$\frac{\mu_w^{\text{Liq},o} - \mu_w^{\text{Sol},o}}{T} = \frac{\Delta \bar{G}_{\text{fus}}}{T} = -R \ln a_w. \quad (38)$$

Differentiating Eq. (38) with respect to a_w ; P , T , and x_i being constant:

$$R \frac{\partial \ln a_w}{\partial a_w} = - \frac{\partial(\Delta \bar{G}_{\text{fus}}/T)}{\partial T} \frac{\partial T}{\partial a_w}. \quad (39)$$

Taking into account that

$$\left. \frac{\partial(\Delta \bar{G}/T)}{\partial T} \right|_P = - \frac{\Delta \bar{H}}{T^2}. \quad (40)$$

Eq. (39) becomes

$$\frac{R}{a_w} = \frac{\Delta \bar{H}_{\text{fus}}}{T^2} \frac{\partial T}{\partial a_w}. \quad (41)$$

Integrating Eq. (41) for water as pure solvent and water as a species in a solution:

$$R \ln a_w = \int_{T_o}^{T_f} \frac{\Delta \bar{H}_{\text{fus}}}{T^2} dT. \quad (42)$$

Using Eqs. (16)–(23), the expression for $\ln a_w$ is:

$$\begin{aligned} \ln a_w = & \ln \left(\frac{\phi_w}{x_w} \right) + \frac{z}{2} q_w \ln \left(\frac{\theta_w}{\phi_w} \right) + \left[\frac{z}{2} (r_w - q_w) - (r_w - 1) \right] \\ & - \frac{\phi_w}{x_w} \left(\sum_{i=1}^n x_i l_i \right) + q_w \left[1 - \ln \left(\sum_{i=1}^n \theta_i \tau_{iw} \right) \right. \\ & \left. - \sum_{i=1}^n \frac{\theta_i \tau_{wi}}{\sum_{j=1}^n \theta_j \tau_{ji}} \right] + \frac{2AM_w}{b^3} \left[(1 + bI^{1/2}) - \frac{1}{(1 + bI^{1/2})} \right. \\ & \left. - 2 \ln(1 + bI^{1/2}) \right] + \ln x_w. \quad (43) \end{aligned}$$

Finally, if the functionality of $\Delta \bar{H}_{\text{fus}}$ with temperature is known (Dougherty & Howard, 1998) and Eq. (42) is integrated, the freezing point of the solution (T_f) can be calculated.

3. Materials and methods

The proposed model was used to predict the thermodynamic properties of aqueous binary solutions of NaCl, KCl, CaCl₂ and ethanol.

3.1. UNIQUAC model parameters

The extended UNIQUAC parameters, q and r , for the study cases were obtained from Thomsen et al. (1996, 2004) (Table 1). Parameters of Eq. (8) were obtained from Thomsen et al. (1996, 2004), and Christensen and Thomsen (2003) (Tables 2 and 3).

Table 1
UNIQUAC q and r parameters (Thomsen et al., 1996, 2004)

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

Table 2
UNIQUAC interaction parameters u_{ji}^o (Thomsen et al., 1996, 2004; Christensen & Thomsen, 2003)

ij	H ₂ O	Na ⁺	K ⁺	Ca ²⁺	Cl ⁻	Ethanol
H ₂ O	0	733.286	535.023	166.7021	1523.39	496.8
Na ⁺		0	-46.194	-182.2332	1443.23	2795.0
K ⁺			0	-402.9549	1465.18	745.4
Ca ²⁺				0	2316.383	-
Cl ⁻					2214.81	1650.0
Ethanol						624.00

Table 3
UNIQUAC interaction parameters u'_{ji} (Thomsen et al., 1996; Thomsen et al., 2004; Christensen & Thomsen, 2003)

ij	H ₂ O	Na ⁺	K ⁺	Ca ²⁺	Cl ⁻	Ethanol
H ₂ O	0	0.4872	0.9936	-5.7699	14.631	0.282
Na ⁺		0	0.1190	-3.3839	15.635	0
K ⁺			0	-3.3100	15.329	1.806
Ca ²⁺				0	9.2428	-
Cl ⁻					8.3194	4.09
Ethanol						0

3.2. Heat capacity

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

$$\begin{aligned} A = & 35.765 + 4.222 \times 10^{-2}(T - 273.15) \\ & + 3.681 \times 10^{-4}(T - 273.15)^2. \quad (44) \end{aligned}$$

Although Eq. (44) was obtained for temperatures above 0 °C, it is assumed that it can be used for temperatures lower than 0 °C. This assumption can be made taking into account the smoothness of A for temperatures above 0 °C (Marion, Kargel, Catling, & Jakubowski, 2005).

The values Cp_i^o and $\bar{C}p_i^\infty$ were estimated as suggested by Thomsen et al. (1996):

$$Cp_i = \delta_{1,i} + \delta_{2,i}T + \frac{\delta_{3,i}}{T - 200}. \quad (45)$$

The parameters $\delta_{1,i}$, $\delta_{2,i}$ and $\delta_{3,i}$ are shown in Table 4. In the case of Ca²⁺, those parameters were obtained by fitting model data to Eq. (45).

Table 4
Parameters for calculating Cp_i (Thomsen et al., 1996)

Species	$\delta_{1,i} \times 10^3$ (J kmol ⁻¹ K ⁻¹)	$\delta_{2,i} \times 10^3$ (J kmol ⁻¹ K ⁻²)	$\delta_{3,i} \times 10^3$ (J kmol ⁻¹)
H ₂ O	58.370	0.03896	523.88
Na ⁺	600.62	-1.1006	-23232
K ⁺	415.09	-0.8142	-16316
Ca ²⁺	-5478.24 ^a	14.433 ^a	75680.34 ^a
Cl ⁻	400.35	-1.1312	-18574
Ethanol	-5.677	0.469	-

^a Value obtained in this work.

3.3. Density

The parameters q_i^P and r_i^P were estimated by the minimization of the following object function:

$$OF = \sum_{data} \left| \frac{\rho^{exp} - \rho^{calc}}{\rho^{exp}} \right| \quad (46)$$

A total of 940 binary experimental data from various sources were used for the parameter estimation.

The solvent density (ρ_s) and the dielectric constant (ϵ_r) depend on pressure (Zafarani-Moattar & Sardroodi, 2003), therefore:

$$A^P = \frac{3}{2}A \left(\frac{1}{3}\beta - \frac{\partial \ln \epsilon_r}{\partial P} \right), \quad (47)$$

where β is the solvent expansion coefficient. ρ_s , ϵ_r , β , and $\partial \ln(\epsilon_r)/\partial P$ can be calculated using the expressions proposed by Brasil Floriano and Chaer Nascimento (2004).

The values of V_i^o and \bar{V}_i^∞ were calculated by:

$$V_i^o = \frac{\delta_{4,i} \left[1 + \left(1 + \frac{T}{\delta_{5,i}} \right)^{\delta_{6,i}} \right]}{\delta_{7,i}}, \quad (48)$$

$$\bar{V}_i^\infty(T) = \delta_{4,i} + \delta_{5,i}T + \delta_{6,i}T^2 + \delta_{7,i}T^3. \quad (49)$$

The coefficients used in Eqs. (48) and (49) are shown in Table 5.

3.4. Freezing point

The expression used for the $\Delta \bar{H}_{fus}$ is (Rahman, 1995):

$$\Delta \bar{H}_{fus} = \lambda_1 + \lambda_2 T + \lambda_3 T^2, \quad (50)$$

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

3.5. Experimental data

The bibliography of experimental data for heat capacity, density and freezing point for the evaluation of the model accuracy and for fitting parameters q^P and r^P is shown in Tables 6–8.

Table 6
Bibliography for heat capacity data

Solute	Range		Reference
	T (°C)	w (kg kg ⁻¹)	
NaCl	-33 to 12	0 to 0.208	Archer and Carter (2000)
NaCl	0 to 40	0 to 0.1	Chen (1982)
NaCl	15 to 45	0 to 0.06	Hess and Gramkee (1940)
NaCl	-10 to 30	0.05 to 0.25	ICT (2003)
NaCl	6 to 57	0.07 to 0.25	Perry et al. (1997)
NaCl	35 to 41	0 a to 0.07	White (1940)
KCl	15 to 45	0 to 0.07	Hess and Gramkee (1940)
KCl	6 to 40	0 to 0.249	ICT (2003)
KCl	6 to 40	0.04 to 0.25	Perry et al. (1997)
KCl	25	0 to 0.157	Randall and Rossini (1929)
KCl	30 to 130	0 to 0.118	Ruterjans et al. (1969)
CaCl ₂	-30 to 40	0 to 0.35	Conde (2004)
CaCl ₂	-40 to 30	0.08 to 0.3	ICT (2003)
Ethanol	3 to 41	0 to 1	ICT (2003)
Ethanol	-20 to 20	0.107 to 0.903	Khan (2004)
Ethanol	3 to 41	0.1 to 1	Perry et al. (1997)

Table 7
Bibliography for density data

Solute	Range		Reference
	T (°C)	w (kg kg ⁻¹)	
NaCl	-20 to 30	0.05 to 0.25	ICT (2003)
NaCl	-20 to 20	0 to 0.26	Mironenko et al. (2001)
NaCl	0 to 100	0.01 to 0.26	Perry et al. (1997)
KCl	0 to 100	0.01 to 0.28	Perry et al. (1997)
KCl	-10.6 to 20	0 to 0.3	Pronk (2006)
KCl	20	0.05 to 0.24	Weast (1974)
CaCl ₂	-30 to 30	0.05 to 0.3	ICT (2003)
CaCl ₂	-5 to 140	0.02 to 0.4	Perry et al. (1997)
CaCl ₂	20	0.05 to 0.4	Weast (1974)
Ethanol	10 to 40	0 to 1	ICT (2003)
Ethanol	-45 to 40	0.025 to 0.95	Khan (2004)
Ethanol	-50 to 20	0 to 0.93	Lugo et al. (2002)
Ethanol	10 to 40	0 to 1	Perry et al. (1997)

Table 5
Coefficients used in Eqs. (48) and (49) for calculating the partial molar volume at infinite dilution and molar volume of pure compounds

Species	$\delta_{4,i}$ (m ³ mol ⁻¹)	$\delta_{5,i}$ (m ³ mol ⁻¹ K ⁻¹)	$\delta_{6,i}$ (m ³ mol ⁻¹ K ⁻²)	$\delta_{7,i}$ (m ³ mol ⁻¹ K ⁻³)	R ²	Reference
H ₂ O	0.30542	647.13	0.081	5.459	-	a
Na ⁺	-6.642 × 10 ⁻²	3.682 × 10 ⁻⁴	-5.040 × 10 ⁻⁷	-	0.990	b
K ⁺	-5.894 × 10 ⁻²	4.019 × 10 ⁻⁴	-5.851 × 10 ⁻⁷	-	0.973	b
Ca ²⁺	-0.5037	4.341 × 10 ⁻³	-1.282 × 10 ⁻⁵	1.248 × 10 ⁻⁸	0.993	b
Cl ⁻	-5.579 × 10 ⁻²	4.622 × 10 ⁻⁴	-7.234 × 10 ⁻⁷	-	0.993	b
Ethanol	0.27627	513.92	0.2331	1.648	-	a

a Perry et al. (1997).

b Parameters obtained by fitting experimental data published by Millero (1971).

Table 8
Bibliography for freezing point data

Solute	Range of w (kg kg ⁻¹)	Reference
NaCl	0 to 0.04	ICT (2003)
NaCl	0 to 0.07	Scatchard and Prentiss (1933)
NaCl	0.01 to 0.23	Weast (1974)
KCl	0.002 to 0.196	ICT (2003)
KCl	0 to 0.08	Scatchard and Prentiss (1933)
KCl	0.005 to 0.13	Weast (1974)
CaCl ₂	0 to 0.324	ICT (2003)
CaCl ₂	0.001 to 0.307	SPT (2003)
CaCl ₂	0.005 to 0.32	Weast (1974)
Ethanol	0 to 0.454	ICT (2003)
Ethanol	0.005 to 0.68	Weast (1974)

4. Results and discussion

4.1. Heat capacity

Fig. 1 illustrates the results obtained in the case of specific heat for the aqueous solutions studied. In the case of

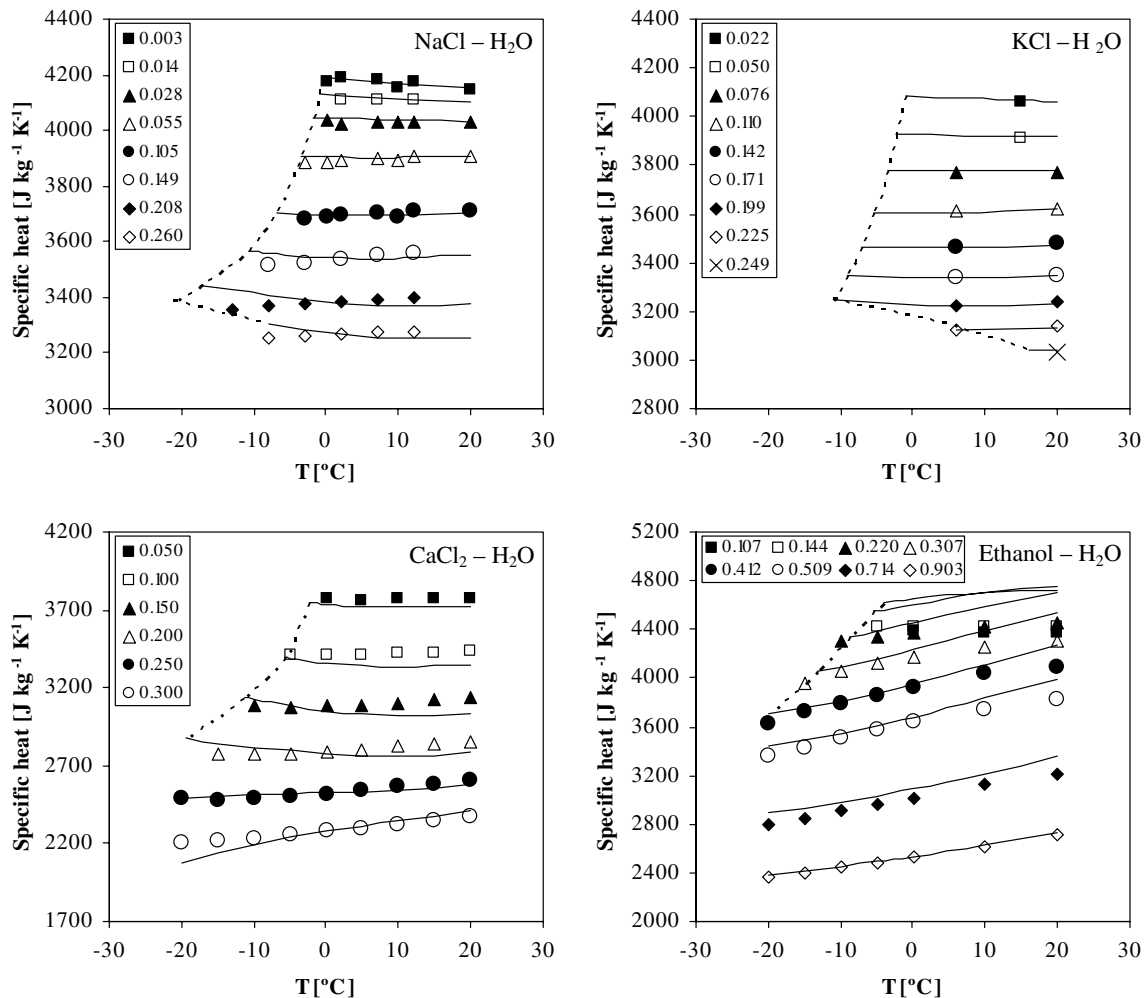


Fig. 1. Specific heat of solutions at different temperatures and solute mass fractions. Symbols correspond to experimental data and lines to calculated values. Dashed lines represent phase equilibria. Sources: NaCl–water: Archer and Carter (2000), KCl–water: ICT (2003), CaCl₂–water: Conde (2004), ethanol–water: Khan (2004).

solutions of electrolytes, it was observed that the lower concentration of solutes and the higher temperature, the better accuracy. It must be taken into account that the parameters q and r were obtained using data at temperatures above 0 °C. In the case of aqueous solutions of ethanol, the experimental data are represented with good accuracy only for high solute concentration. This kind of system may present associative interactions (Ferreira, Macedo, & Bottini, 2005; Pessôa Filho, Mohamed, & Maurer, 2005), which were not considered in the extended UNIQUAC model. Other functionality of u_{ji} with temperature may improve the prediction accuracy for low ethanol concentrations (Demirel, Geceğörmez, & Paksoy, 1992; Demirel & Paksoy, 1992, 1997).

4.2. Density

Values of q^P and r^P obtained by fitting the model to experimental data are shown in Table 9. The model presented in this paper reproduced accurately the density data

Table 9

Parameters q^P and r^P obtained by fitting the experimental data to the model

Species	Parameter (Pa^{-1}) ($\times 10^{12}$)	
	q^P	r^P
H ₂ O	-386.27	-153.51
Na ⁺	-1443.19	1141.13
Ca ²⁺	118.45	524.91
K ⁺	-1463.36	-238.44
Cl ⁻	1.932	145.06
Ethanol	-1124.56	-1502.39

(Fig. 2). The model predicted density similarly to the case of heat capacity. However, in the case of aqueous solutions of ethanol, good accuracy was observed over the entire composition range.

4.3. Freezing point

The experimental and calculated freezing points of the aqueous solutions studied are shown in Fig. 3. For electro-

lyte solutions, the predictions are very good in the whole concentration range. For the aqueous CaCl₂ solution, the model predicts freezing point with less accuracy when solution concentration is closer to the eutectic point. In the case of aqueous ethanol solution, the model does not predict neither the values nor the behavior when mass fractions are larger than 0.1. The experimental behavior may be related to the associative interactions (Skjold-Jørgensen, Rasmussen, & Fredenslund, 1982), which are not predicted by the model.

4.4. Mean percent error

The mean percent error (MPE) was defined as follows:

$$MPE = \frac{100}{N} \sum_{data} \left| \frac{y^{exp} - y^{calc}}{y^{exp}} \right| \quad (51)$$

The MPE values for the studied properties taking into account the experimental values obtained from the bibliography are shown in Fig. 4. For heat capacity, density and

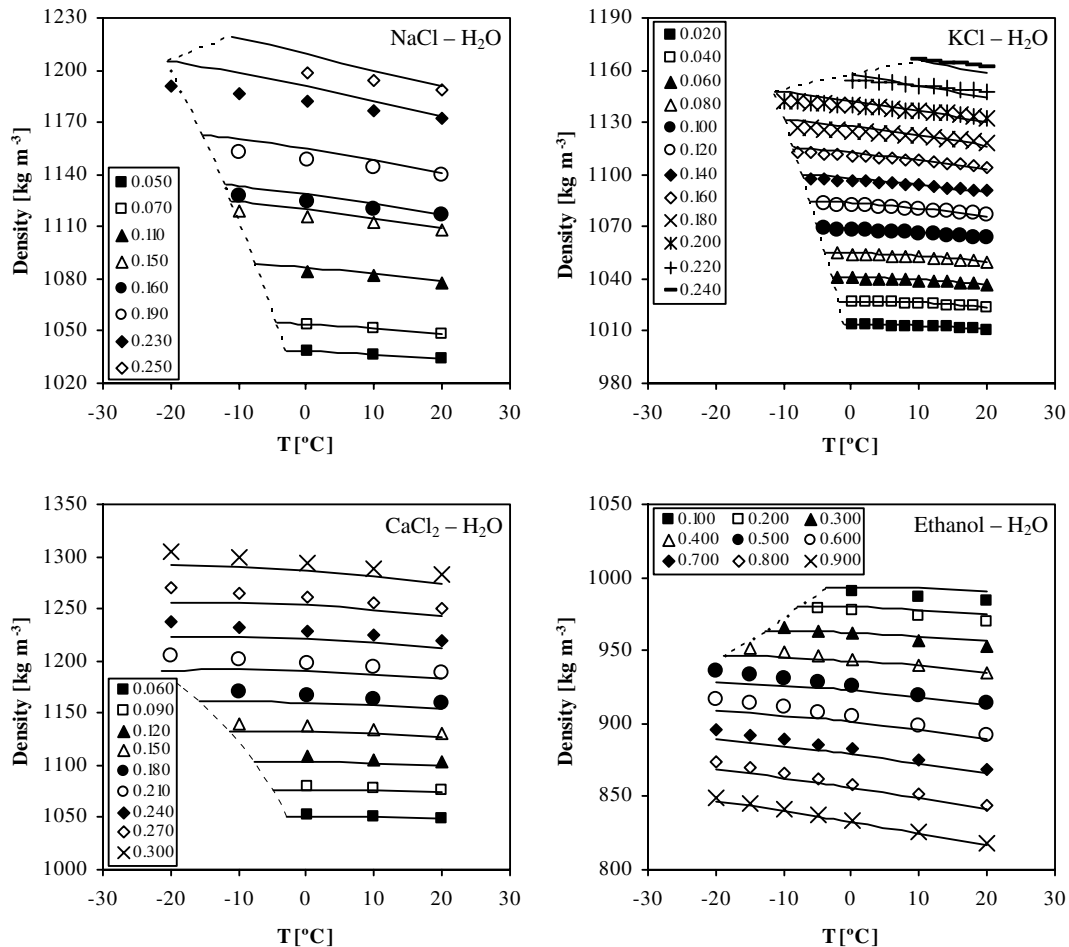


Fig. 2. Density of solutions at different temperatures and solute mass fractions. Symbols correspond to experimental data and lines to calculated values. Dashed lines represent phase equilibria. Sources: NaCl-water: ICT (2003), KCl-water: Pronk, 2006; CaCl₂-water: ICT (2003), ethanol-water: Khan (2004).

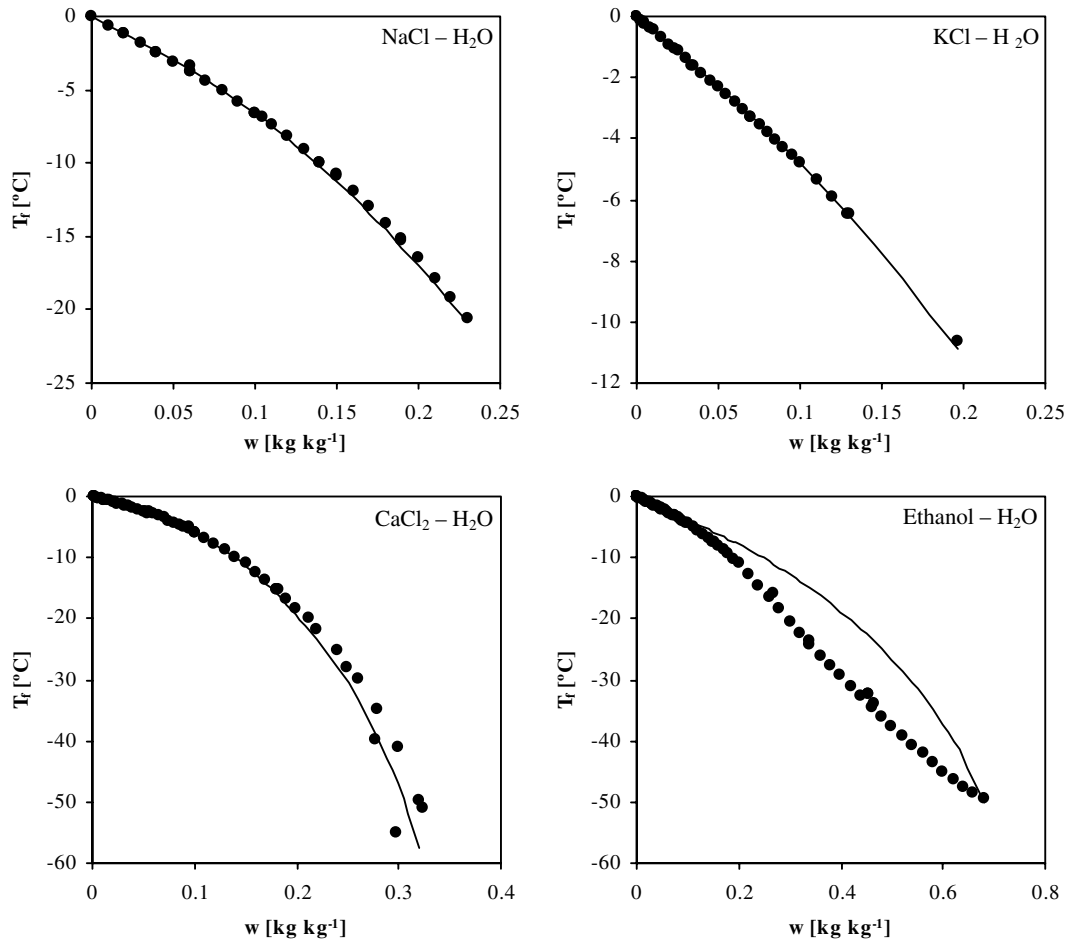


Fig. 3. Freezing points at different solute mass fractions. Symbols correspond to experimental data and lines to calculated values. Sources: NaCl–water: Weast (1974), Scatchard and Prentiss (1933), KCl–water: Weast (1974) and ICT (2003), CaCl₂–water: ICT (2003) and SPT (2003), ethanol–water: Weast (1974) and ICT (2003).

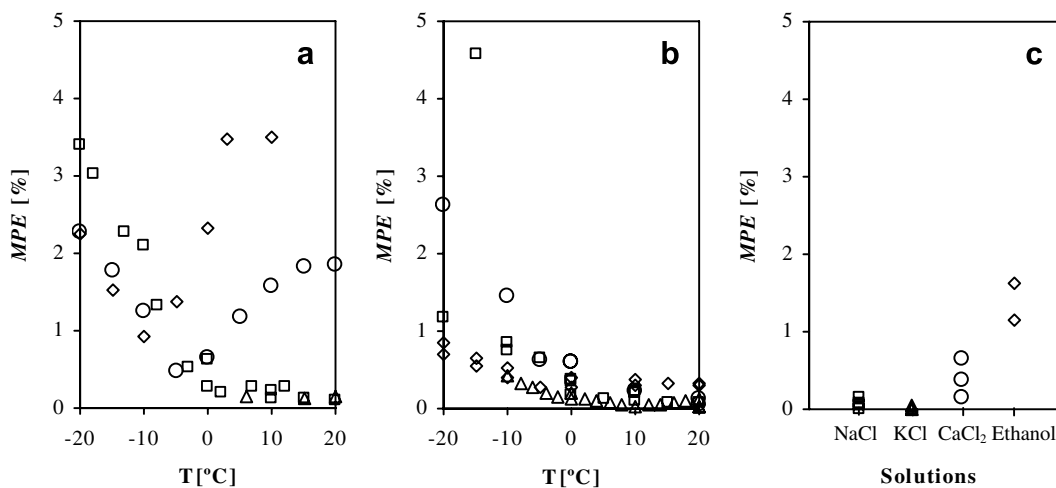


Fig. 4. Mean percent errors for the studied properties considering the bibliography used. (a) Heat capacity, (b) density and (c) freezing point. (□) NaCl–water, (△) KCl–water, (○) CaCl₂–water and (◇) ethanol–water.

freezing temperature the *MPE* were less than 4%, 5%, and 2%, respectively. In the case of heat capacity and density, at temperatures below 0 °C, it can be observed that the

lower temperature, the higher *MPE*. Moreover, in general *MPE* were higher for aqueous solutions of ethanol and CaCl₂.

5. Conclusions

A thermodynamic model of excess Gibbs energy was presented for predicting heat capacity, density and freezing point of liquid refrigerants used in chilling and freezing of foods. New model parameters for predicting volume properties were estimated. In general, the errors obtained were small but increased at temperatures below 0 °C. That increment may be related to the fact that the binary interaction parameters used were fitted for a temperature range above 0 °C and therefore, higher extrapolation errors may be expected in the temperature range of liquid refrigerants.

Taking into account the promising results obtained, at present, the application of the model for ternary aqueous systems commonly used in chilling and freezing of foods is a subject of current study in our research group.

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