Melting temperature depression caused by high pressure gases. Effect of the gas on organic substances and on ionic liquids

José O. Valderrama [a,b,*], Pedro F. Arce [c]

[a] University of La Serena, Faculty of Engineering, Department of Mechanical Engineering, P.O. Box 554, La Serena, Chile
[b] Center for Technological Information (CIT), c/Monseñor Subercaseaux 667, La Serena, Chile
[c] University of São Paulo, Engineering School of Lorena, Campus I, P.O. Box 116, Lorena, SP, Brazil

ABSTRACT

The effect on the melting temperature depression (MTD) of organic substances and ionic liquids caused by different types of pressurizing gases is analyzed. A high pressure gas produces a combined effect between solubility and pressure that causes the melting temperature to decrease. The authors have previously used phase equilibrium relations to correlate MTD of organic substances and ionic liquids under high pressure carbon dioxide, but other gases were not considered. The Peng–Robinson equation of state with the Wong–Sandler mixing rules showed to be appropriate for correlating the phase equilibrium in these high pressurized systems and is the model used is in this work. Three organic substances (naphthalene, biphenyl and octacosane) under high pressure produced by three gases (ethane, ethylene and carbon dioxide) for which experimental data on MTD are available were considered in this study. Then extension to an ionic liquid under high pressure carbon dioxide and high pressure ethylene was done. The proposed thermodynamic method and the model used show to have the necessary flexibility to acceptably correlate the MTD produced in these systems.

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1. Introduction

Pure crystalline solids have a characteristic melting temperature, which is expressed as the temperature at which the solid melts to become a liquid. Pure crystalline substances have a clear and sharply defined melting temperature. During the phase change process, all energy added to the substance is consumed as heat of fusion, and the temperature remains constant, at a given pressure. The experimental determination of the melting temperature is relatively simple and is used in many areas of chemistry to obtain a first impression of the purity of a substance. This is because even small quantities of impurities change the melting temperature, or at least clearly enlarge its melting range [1]. Extensive collections of tables and handbooks give the exact values of melting temperature of many pure inorganic and organic substances [1,2].

The melting temperature T_m is a fundamental physicochemical property of a molecule that is controlled by both single-molecule properties and intermolecular interactions due to packing in the solid state [3]. It finds applications in chemical identification,

purification, and calculations of a number of other physicochemical properties such as vapor pressure and aqueous solubility [4]. However because of the complex influence of energy and entropy factors, melting temperatures are difficult to predict.

For a pure substance, if the pressure increases the melting temperature usually increases (except for water, for instance, which has a different behavior at certain ranges of temperature). However, if a liquid substance is in contact with a high pressure soluble gas, the solid–liquid–gas equilibrium is established at a temperature below the melting temperature of the pure liquid. This phenomenon is not new and in fact may be produced by several factors such as mixture with another component, by size reduction or by exerting pressure with a soluble gas [5]. In the latter case, when the pressure of the gas increases, it could also happen that the melting temperature decreases, goes through a minimum and then increases again.

The phenomenon of MTD has been widely studied for organic compounds such as aromatics, polymers and lipids. Hammam and Sivik [6] tested a series of glycerides that showed a melting point depression of 15–25 °C in the presence of high pressure carbon dioxide. Similar behavior of solid lipids was noticed by Sampaio de Sousa and co-workers [7] who found T_m decrease up to 13 °C. Fukné-Kokot et al. [8] determined MTD of several organic solids under high pressure CO_2 while Fujiwara et al. [9] observed a remarkable lowering of T_m for semicrystalline of poly(lactide) in supercritical CO_2. The gas-induced MTD has been also observed

* Corresponding author at: University of La Serena, Faculty of Engineering, Department of Mechanical Engineering, P.O. Box 554, La Serena, Chile. Tel.: +56 51 551158; fax: +56 51 551158.
E-mail addresses: jvalderr@userena.cl, citchile@entelchile.net (J.O. Valderrama).

Notation

Symbols

a_i, b_i	constants for component "i" in the PR EoS
a_m, b_m	mixture constants in PR EoS
A_{12}, A_{21}	van Laar parameters
f	fugacity
F	objective function Eq. (7)
G^E	excess Gibbs free energy
k_{ij}	binary interaction parameter
N	number of experimental data points
n_i	number of moles of component i
P	melting pressure
P_c	critical pressure
R	gas universal constant
T	melting temperature
T_m	normal melting temperature
T_c	critical temperature
T_r	reduced temperature
x	mole fraction in liquid phase
y	mole fraction in gas phase
Z	compressibility factor

Abbreviations

EoS	equation of state
IL, ILs	ionic liquid, ionic liquids
MTD	melting temperature depression
PR/WS/VL	Peng–Robinson/Wong–Sandler/Van Laar
WS	Wong–Sandler
ΔS_m	entropy of fusion at T_m
$\%\Delta T_m$	% deviation between correlated and experimental melting temperature
$\lvert\%\Delta T_m\rvert$	absolute % deviation between correlated and experimental melting temperature

Greek letters

ϕ	fugacity coefficient
ω	acentric factor
ξ	mole fraction (any phase)

Superindex

G,L,S	gas, liquid, solid
SCL	sub-cooled liquid

in ionic liquids (ILs) but has received special attention in the last few years only, especially after discovering MTD higher than $100\,°C$ for some ILs. The MTD of ILs would allow the use of ILs that has relatively high melting temperatures (say around 70–$130\,°C$) as solvents at room temperatures. A little before the 1990s two reports about MTD in the presence of carbon dioxide in ionic salts could be found [10,11]. Years later, Kazarian et al. [12] observed liquid-crystal transition for [C$_{16}$mim][PF$_6$] with carbon dioxide These authors found that high pressure carbon dioxide induced melting point depression in the range of what it was found for other organic solids, that is not higher than $25\,°C$. More recently, Scurto and Leitner [13] reported that high pressure carbon dioxide can induce surprisingly high melting temperature depression, up to $120\,°C$.

Scurto et al. [14] described the phenomenon of MTD and presented a general pressure-temperature diagram of a highly asymmetric system for an organic compound and a compressed gas. The phenomenon is similar to that of organic compounds under high pressure gases but that, according to Scurto and Leitner [13] did not received much attention until ILs were discovered to have exceptional characteristics as reaction media for many reactions.

The melting temperature depression caused by a high pressure gas that dissolves in the liquid is a complex physicochemical process in which van der Waals forces and electrostatic interaction forces compete in some way. The impact of the two forces plays different roles for different kinds of substances and especially for ILs. From a thermodynamic point of view, which is of interest in this paper, the phenomenon is a phase equilibrium situation in which the three phases are present with two substances involved [14]. Therefore equilibrium equations can be formulated at the new melting temperature in which the pure solid will form.

In this paper, the effects of three pressurizing gases (ethane, ethylene and carbon dioxide) on the melting temperature depression (MTD) of three substances of organic type (naphthalene, biphenyl and octacosane) and one ionic liquid ([TBAm][BF$_4$]), hereafter named as "substances", are analyzed. The thermodynamic model used is described in what follows.

2. The thermodynamic model

For calculating the MTD, experimental data (melting temperature vs. pressure) were modeled using the fundamental equation of phase equilibrium for the different phases present. That is the equality of fugacities of each component in the different phases. For the variables given, three equilibrium equations are needed: gas–liquid equilibrium for both components (the gas and the substance) and solid–gas equilibrium for the substance (hydrocarbons or ionic liquid). It is assumed that no gas is dissolved in the solid phase of the substance. The concentration of the substance in the gas phase (y_2) was maintained as a variable to be calculated, so the solid–gas equilibrium which includes the melting temperature could be applied and the system of equations solved together with the other equilibrium relations.

In the equilibrium relations, expressed through the equality of fugacities, an equation of state was used to calculate the required fugacities. The Peng–Robinson (PR) equation of state (EoS) was used [15] with the Wong–Sandler (WS) mixing rules [16] The van Laar model (VL) [17] was incorporated into the mixing rules of the WS model. The model is designated hereafter as PR/WS/VL and is summarized in Table 1. In the first column the PR equation and the WS mixing rules are shown while in the second column the equations that describe the fugacity coefficient are presented.

Therefore, the following three phase equilibrium equations are written:

$$f_2^G = f_2^S \tag{1}$$

$$f_1^G = f_1^L \tag{2}$$

$$f_2^G = f_2^L \tag{3}$$

In these equations f represents the fugacity, subscript 1 represents the pressurizing gas and subscript 2 represents the substance. The superscripts S, L and G represent the solid, liquid and gas, respectively. The fugacities are expressed in terms of the fugacity coefficients as follows:

a) for the solid–gas equilibrium of component 2 (the substance to de solidified) the fugacity of the solid can be written to a good approximation as follows [17]:

$$y_2\phi_2^G P = f_2^{SCL}\exp\left[\frac{\Delta S_m}{R}\left\{1 - \frac{T_m}{T}\right\}\right] \tag{4}$$

b) for the gas–liquid equilibrium the following equation can be written for the high pressure gas (designated as component 1), Eq. (2) is:

$$y_1\phi_1^G = x_1\phi_1^L \tag{5}$$