



# Calculation of CO<sub>2</sub> freezing points in mixtures using SRK and PR EoSs

## 使用 SRK 和 PR 状态方程计算混合物中二氧化碳的凝固点

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**Abstract** - Global greenhouse gas (GHG) emissions have grown in comparison to pre-industrial levels. Under this scenario, several solutions have been suggested to reduce GHG emissions. Carbon dioxide capture and storage (CCS) is one of the key mitigation actions that have been proposed to meet this goal. Capture of CO<sub>2</sub> can be effectively applied to large point sources, like natural gas production facilities, in order to separate CO<sub>2</sub> from other gaseous products as a concentrated stream which can be readily transported to a storage site. Cryogenic CO<sub>2</sub> removal methods have been widely studied recently as a technology which offers some advantages in comparison with conventional solutions in case of those natural gas reserves that were previously considered uneconomic due to the presence of significant amounts of acidic gas components (carbon dioxide and hydrogen sulfide). Furthermore, cryogenic CO<sub>2</sub> removal methods can capture CO<sub>2</sub> in a liquid form, making its geological storage relatively easy. Some cryogenic removal technologies are based on the formation of solid CO<sub>2</sub> while in other processes particular attention is required to avoid the formation of dry ice. As a result, in both cases, it is necessary to be able to predict the conditions at which CO<sub>2</sub> can freeze-out. A thermodynamic method has been proposed for modeling the solubility of carbon dioxide in pure light hydrocarbons and hydrogen sulfide and in multicomponent mixtures. It is based on the use of a cubic equation of state (EoS) for the calculation of fugacity coefficients in the liquid and vapor phases. The Soave-Redlich-Kwong and the Peng-Robinson EoSs have been chosen in this work since they are widely used in natural gas processing systems. As for the fugacity of CO<sub>2</sub> as a pure component in the solid phase, it is expressed in terms of proper regressed parameters (enthalpy of fusion, specific heat difference between liquid and solid and melting temperature) of the freezing component. The focus is a detailed analysis of the method performances by means of a comparison with experimental data, when available. The addition of hydrogen sulfide and nitrogen to the CO<sub>2</sub>-containing mixture is studied to understand how they affect carbon dioxide freezing points.

**Keywords** – Carbon dioxide, Freeze-out, Solubility, SRK, PR

### I. INTRODUCTION

Climate change is definitely one of the most serious challenges to be faced. Since pre-industrial times atmospheric greenhouse gas (GHG) concentrations have markedly increased as a result of increasing emissions of GHGs due to human activities. In particular, total anthropogenic GHG emissions reached the highest levels in human history from 2000 to 2010 at an average rate of 2.2% per year compared to 1.3% per year between 1970 and 2000. Among all major direct GHGs related to human activities, CO<sub>2</sub> from fossil fuel combustion and in industrial processes plays a significant role, with 76% of total GHG emissions in 2010 [1]. In this scenario, mitigation strategies are intended to stabilize GHG concentrations in the atmosphere at a level to prevent harmful consequences on either human or ecological well-being. With respect to the energy supply sector, these strategies include options to mitigate GHG emissions from the extraction, transport and conversion of fossil fuels through CO<sub>2</sub> capture and storage (CCS). This would allow fossil fuels to continue to be used in the future, without significantly contributing to climate change. Many technologies currently exist for separation and capture of CO<sub>2</sub> from gas streams in power plants [2]. They are often classified into oxyfuel, pre- and post-combustion processes. Post-combustion processes are considered the most realistic technology [3] in the short term because they can be retrofitted to already operating power plants and industries. Several post-combustion processes have been developed, including physical and/or chemical absorption, adsorption, membranes and cryogenics, depending on the characteristics of the flue gas stream. The use of cryogenic processes is worth considering when the concentration of CO<sub>2</sub> in the flue gas is high [4]. They are also of great interest in the natural gas purification industry for the removal of CO<sub>2</sub> to produce what is known as pipeline quality

natural gas. In particular, cryogenic technologies allow to exploit also those gas reserves that were considered uneconomic in the past due to the high content of acidic components. Nowadays they have been taken into consideration to face the extensive switching from coal to gas as a way for a reduction of GHG emissions. For all these reasons, great attention has been recently devoted to low-temperature processes which possess many potential advantages, including the production of liquid CO<sub>2</sub> which can be readily transported by pipeline. Some cryogenic processes can be classified as solid-based CO<sub>2</sub> capture processes. Some examples are CO<sub>2</sub> capture by anti-sublimation [5], the Controlled Freeze Zone<sup>TM</sup> technology (CFZ<sup>TM</sup>) [6] and the cryogenic CO<sub>2</sub> capture (CCC) process [7]. On the contrary, other cryogenic processes avoid the formation of dry ice. The Ryan-Holmes process, for example, avoids solids formation in a cryogenic distillative separation of acid gases by adding a solids-preventing agent such as one or more C<sub>2</sub>-C<sub>5</sub> alkanes [8]. A novel distillation process [9] eliminates solid CO<sub>2</sub> build-up by performing distillation in two columns operated at high and low pressures, respectively. In all these processes the prediction of CO<sub>2</sub> freezing points is key for process design. In the literature it has been reported that unreliable CO<sub>2</sub> freezing predictions are being made by several of the commercial process simulators typically used by gas processors [10]. Therefore, the aim of the work is to provide a reliable thermodynamic tool for accurately predicting CO<sub>2</sub> freezing points.

## II. THERMODYNAMIC FRAMEWORK

Some empirical correlations based on CO<sub>2</sub> freeze-out experiments have been developed to predict the liquid freezup curves [11]. However, they are not trustable enough to be used for industrial applications. The typical approach for performing every kind of equilibria calculations is based on equating partial fugacities for each component in each phase. In the case of solid-liquid-vapor equilibria calculations (SLVE), Eq. (1)-(3) hold at equilibrium:

$$f_i^S(T, P) = \hat{f}_i^L(T, P, \underline{x}) \quad (1)$$

$$f_i^S(T, P) = \hat{f}_i^V(T, P, \underline{y}) \quad (2)$$

$$\hat{f}_i^L(T, P, \underline{x}) = \hat{f}_i^V(T, P, \underline{y}) \quad (3)$$

where  $f_i^S(T, P)$ ,  $\hat{f}_i^L(T, P, \underline{x})$  and  $\hat{f}_i^V(T, P, \underline{y})$  stand for the fugacity of component  $i$  in the solid, liquid and vapor phase, respectively.

Two approaches are typically used to solve equilibria calculations: the activity coefficient or the equation of state (EoS) approach. They basically differ for the way in which the partial fugacity in the liquid phase is expressed, which affects the form of Eq. (1) either for SLE or SLVE calculations.

The activity coefficient approach has been used in several papers which deal with SLE calculations and consequently involve Eq. (1) only, which is written as:

$$f_i^S(T, P) = \gamma_i x_i f_i^L(T, P) \quad (4)$$

Therefore, the activity coefficient approach requires the estimation of the activity coefficient,  $\gamma_i$ , for the solubility,  $x_i$ , to be found. Myers and Prausnitz [12] have calculated the activity coefficient from Scatchard's equation [13] to describe the equilibrium between pure solid CO<sub>2</sub> and a saturated solution of CO<sub>2</sub> in a liquid solvent. The same equation has been used by Preston and Prausnitz [14], Dixon and Johnston [15] and Shen and Lin [16] for obtaining liquid-phase activity coefficients. On the contrary, Gmehling et al. [17] have estimated the activity coefficient from the group-contribution method UNIFAC, while Eggeman and Chafin [18] have chosen the Non-Random Two-Liquid (NRTL) equation.

Eggeman and Chafin [18] have also studied the equation of state approach either for SLE or for SVE calculations. When the equation of state approach is used, Eq. (1) is rewritten as:

$$f_i^S(T, P) = P x_i \hat{\phi}_i^L(T, P, \underline{x}) \quad (5)$$

They have chosen a standard form of the Peng-Robinson (PR) equation of state to calculate fugacity coefficients, with binary interaction parameters  $k_{ij}$ s derived from VLE regressions. The same equation of state has been selected by ZareNezhad and Eggeman [11] for predicting CO<sub>2</sub> freezing points of hydrocarbon liquid (SLE) and vapor (SVE) mixtures. However, in this case  $k_{ij}$ s have been assumed to be temperature-dependent and this dependency has been found by minimization of the difference between experimental and calculated freezing temperatures. Shen and Lin [16] have used both the PR and the Soave-Redlich-Kwong (SRK) equations of state to calculate the solubility of carbon dioxide in saturated liquid methane. The equation of state approach has been also preferred by Ferioiu et al. [19], Xu et al. [20], Yazdizadeh et al. [21, 22] and Kikic et al. [23] to calculate the solubility of solid compounds in supercritical fluids. For modeling solid-fluid equilibria at high pressures also Seiler et al. [24] have decided to describe the non-ideality of the liquid phase by means of an equation of state, that is the SAFT equation of state. Tang and Gross [25] have used the same equation reported by Seiler et al. [24], but they have used the PCP-SAFT equation of state instead.

In this work, cubic equations of state with proper adaptive parameters have been applied to predict CO<sub>2</sub> freezing points in systems containing hydrocarbons, hydrogen sulfide and nitrogen.

## III. PROPOSED METHOD

In this work, the equation of state approach has been chosen in order to describe the solid-liquid-vapor equilibrium which may establish in some cryogenic processes aimed at removing CO<sub>2</sub> from gaseous streams. Equilibria calculations are based on the equality (Eq. (6)) between the fugacity of CO<sub>2</sub> (i.e., the freezing component) in the solid phase and its fugacity in the liquid phase, at the system temperature and bubble pressure. The partial fugacity in the liquid phase is expressed in terms of the fugacity coefficient as in the right-hand side of Eq. (6),

which is obtained by means of an EoS. The SRK [26] and PR [27] EoSs have been used for comparison.

$$f_{CO_2}^S(T, P) = P \cdot x_{CO_2} \cdot \hat{\phi}_{CO_2}^L(T, P, \underline{x}) \quad (6)$$

The pressure in Eq. (6) is the bubble pressure calculated according to Eq. (3), since a three-phase (SLV) equilibrium is considered.

The fugacity of CO<sub>2</sub> in the solid phase can be written taking into account the rigorous thermodynamic relation which allows to express it as a function of the fugacity in the liquid phase, at the same temperature and pressure. By integrating the definition of the fugacity of a pure component introduced by Lewis between the liquid and solid phase at the system temperature and pressure (that is the bubble pressure in case of SLVE calculations) and by substituting the chemical potential of the pure component with the molar Gibbs free energy, the molar Gibbs energy change Δg<sub>L→S</sub>(T,P) for pure CO<sub>2</sub> in going from the liquid to the solid phase can be related to the fugacities in the corresponding phases:

$$\Delta g_{L \rightarrow S}(T, P) = RT \ln \left( \frac{f_{CO_2}^S(T, P)}{f_{CO_2}^L(T, P)} \right) \quad (7)$$

The left-hand side of Eq. (7) can be related to the corresponding enthalpy and entropy changes by:

$$\Delta g_{L \rightarrow S}(T, P) = \Delta h_{L \rightarrow S}(T, P) - T \Delta s_{L \rightarrow S}(T, P) \quad (8)$$

The thermodynamic cycle in Fig. 1 provides a method to evaluate the enthalpy and entropy changes in Eq. (8).

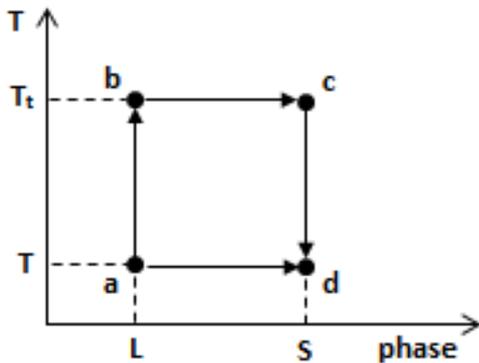


Fig.1, Thermodynamic cycle for the derivation of an expression for the ratio  $f_i^S(T,P)/f_i^L(T,P)$ .

Since both the enthalpy and entropy are state functions, the change between two states depends only on the initial and final state of the system but does not depend on the way in which the system acquires those states. Therefore, the enthalpy change can be calculated according to Eq. (9) by following the path  $a \rightarrow b \rightarrow c \rightarrow d$ , where  $T_t$  represents the triple point temperature.

$$\begin{aligned} \Delta h_{L \rightarrow S}(T, P) &= \Delta h_{a \rightarrow b} + \Delta h_{b \rightarrow c} + \Delta h_{c \rightarrow d} \\ &= \int_T^{T_t} c_p^L(T) dT - \Delta h_m(T_t) + \int_{T_t}^T c_p^S(T) dT \\ &= \int_T^{T_t} [c_p^L(T) - c_p^S(T)] dT - \Delta h_m(T_t) \end{aligned} \quad (9)$$

Similarly, the entropy change can be calculated according to Eq. (10).

$$\begin{aligned} \Delta s_{L \rightarrow S}(T, P) &= \Delta s_{a \rightarrow b} + \Delta s_{b \rightarrow c} + \Delta s_{c \rightarrow d} \\ &= \int_T^{T_t} \frac{c_p^L(T)}{T} dT - \frac{\Delta h_m(T_t)}{T_t} + \int_{T_t}^T \frac{c_p^S(T)}{T} dT \\ &= \int_T^{T_t} \frac{c_p^L(T) - c_p^S(T)}{T} dT - \frac{\Delta h_m(T_t)}{T_t} \end{aligned} \quad (10)$$

As reported by [28], some simplifications can be made. Firstly, the difference between the liquid and solid heat capacities can be assumed to be constant. Secondly, the triple point temperature can be substituted by the normal melting temperature, since for most substances there is little difference between the two, as for the enthalpies of fusion at these two temperatures. Therefore, under these assumptions, the ratio of the fugacity of CO<sub>2</sub> in the solid and liquid phase in Eq. (7) can be expressed as follows:

$$\begin{aligned} \ln \frac{f_{CO_2}^S(T, P)}{f_{CO_2}^L(T, P)} &= \frac{\Delta h_m}{RT_m} \left( 1 - \frac{T_m}{T} \right) + \\ &\quad \frac{\Delta c_p (T_m - T)}{RT} - \frac{\Delta c_p}{R} \ln \frac{T_m}{T} \end{aligned} \quad (11)$$

Eq. (11), also reported by Soave [29], can be combined with Eq. (6), leading to the final result for the freezing point of CO<sub>2</sub> in a mixture at the triple point, which depends only on the properties of the solute (Eq. (12)).

$$x_{CO_2} = \frac{\hat{\phi}_{CO_2}^L(T, P) \exp \left[ \frac{\Delta h_m}{RT_m} \left( 1 - \frac{T_m}{T} \right) + \frac{\Delta c_p}{R} \left( \frac{T_m}{T} - 1 - \ln \frac{T_m}{T} \right) \right]}{\hat{\phi}_{CO_2}^L(T, P, \underline{x})} \quad (12)$$

#### IV. ADAPTIVE PARAMETERS

As shown in Eq. (11), the fugacity of CO<sub>2</sub> in the solid phase strongly depends on its heat of fusion, Δh<sub>m</sub>, on the difference between its liquid and solid heat capacities and on its melting temperature, T<sub>m</sub>. These physical quantities have been assumed as adaptive parameters and have been determined by regression of experimental data of sublimation temperature and solid vapor pressure [30-33]. The regressed parameters have been obtained by minimization of the following objective function:

$$f_{ob} = \sum_{j=1}^{N_{pt}} err_j^2 \quad (13)$$

where  $N_{pt}$  is the total number of points and  $err_j$  is calculated as:

$$err_j = \ln f_{CO_2}^S(T_j, P_j) - \ln f_{CO_2}^L(T_j, P_j) - \left[ \frac{\Delta h_m}{RT_m} \left( 1 - \frac{T_m}{T_j} \right) + \frac{\Delta c_p (T_m - T_j)}{RT_j} - \frac{\Delta c_p}{R} \ln \frac{T_m}{T_j} \right] \quad (14)$$

The regressed values, which depend on the EoS chosen for calculations, are reported in Table 1, along with experimental data [34-36] for a comparison aimed at verifying the physical congruity of the proposed method.

TABLE 1, PARAMETERS INVOLVING PROPERTIES OF THE SOLID PHASE

Parameters	SRK EoS	PR EoS	Exp.
$\Delta h_m/R/T_m$	4.5769	4.6774	4.6266 [36]
$\Delta c_p/R$	1.4792	0.9179	1.7145 [34]
$T_m$ (K)	216.39	216.16	216.59 [35]

The values of  $\Delta h_m/R/T_m$  and  $T_m$  are in good agreement with experimental data, whereas a higher discrepancy has been found for  $\Delta c_p/R$ , especially for the PR EoS. However, in our opinion, the obtained values can be considered physically consistent and they have been used in the following for SLVE calculations.

Also binary interaction parameters have been assumed as adaptive parameters in order to improve the description of the thermodynamic behavior of systems involving the solid phase. New values of  $k_{ij}$ s (Table 2) for both SRK and PR EoSs have been obtained by regression of experimental solubility data of binary mixtures containing CO<sub>2</sub> and *n*-alkanes at low temperatures [37]. Also the value of the binary interaction parameters for the CO<sub>2</sub>-H<sub>2</sub>S pair has been optimized by regression of experimental data [35] of vapor and liquid composition along V-L-CO<sub>2, solid</sub> locus for this pair of compounds. The regressed parameters have been obtained by minimization of the same objective function as in Eq. (13), but this time  $err_j$  is calculated as:

$$err_j = |x_{j,calc} - x_{j,exp}| \quad (15)$$

TABLE 2, OPTIMIZED VALUES OF BINARY INTERACTION PARAMETERS OBTAINED WITH THE PROPOSED METHOD FOR SRK EOS AND PR EOS

Mixture	SRK EoS	PR EoS
CO <sub>2</sub> -C1	0.1243	0.1230
CO <sub>2</sub> -C2	0.1332	0.1281
CO <sub>2</sub> -C3	0.1235	0.1185
CO <sub>2</sub> -C4	0.1150	0.1109
CO <sub>2</sub> -C5	0.1067	0.1007
CO <sub>2</sub> -C6	0.1021	0.0991
CO <sub>2</sub> -H <sub>2</sub> S	0.1020	0.0992

In this work  $k_{ij}$ s for hydrocarbon-hydrocarbon pairs have been taken from ASPEN HYSYS® [38], as well as those for the H<sub>2</sub>S-hydrocarbon pairs and for the N<sub>2</sub>-CH<sub>4</sub> pair. They are reported in Table 3. It is worth noticing that  $k_{ij}$ s for

hydrocarbon-hydrocarbon pairs have the same values for the SRK and PR EoSs.

TABLE 3, VALUES OF BINARY INTERACTION PARAMETERS TAKEN FROM ASPEN HYSYS® [38] FOR PAIRS OTHER THAN THOSE INVOLVING CARBON DIOXIDE

Mixture	SRK EoS	PR EoS
C1-C2	0.0022	0.0022
C1-C3	0.0068	0.0068
C1-C4	0.0123	0.0123
C1-C5	0.0179	0.0179
C1-C6	0.0235	0.0235
C1-H <sub>2</sub> S	0.0888	0.0850
C1-N <sub>2</sub>	0.0312	0.0360
C2-C3	0.0013	0.0013
C2-C4	0.0041	0.0041
C2-C5	0.0076	0.0076
C2-C6	0.0114	0.0114
C2-H <sub>2</sub> S	0.0862	0.0840
C3-C4	0.0008	0.0008
C3-C5	0.0027	0.0027
C3-C6	0.0051	0.0051
C3-H <sub>2</sub> S	0.0925	0.0750
C4-C5	0.0005	0.0005
C4-C6	0.0019	0.0019
C4-H <sub>2</sub> S	0.0626	0.0600
C5-C6	0.0004	0.0004
C5-H <sub>2</sub> S	0.0709	0.0650
C6-H <sub>2</sub> S	0.0570	0.0600

## V. FREEZING POINTS OF CO<sub>2</sub> IN BINARY MIXTURES

The composition of the liquid phase along solid-liquid-vapor locus of binary mixtures containing CO<sub>2</sub> obtained by means of the proposed method has been compared with experimental data available in the literature. Such data have been collected by Kurata [37] from other literature sources [39-42]. The calculated liquid molar fraction of carbon dioxide is in good agreement with experimental data, as shown by the values of Average Absolute Deviation (AAD) reported in Table 4 and calculated according to the following equation:

$$AAD = \frac{\sum_{j=1}^{N_{pt}} |x_{j,calc} - x_{j,exp}|}{N_{pt}} \quad (16)$$

TABLE 4, AVERAGE ABSOLUTE DEVIATIONS OBTAINED WITH THE PROPOSED METHOD, BOTH WITH SRK EOS AND PR EOS, FOR BINARY MIXTURES

Mixture	AAD SRK EoS	AAD PR EoS
CO <sub>2</sub> -C1	0.0374	0.0391
CO <sub>2</sub> -C2	0.0122	0.0118
CO <sub>2</sub> -C3	0.0274	0.0259
CO <sub>2</sub> -C4	0.0340	0.0316
CO <sub>2</sub> -C5	0.0543	0.0537
CO <sub>2</sub> -C6	0.0706	0.0698
CO <sub>2</sub> -H <sub>2</sub> S	0.0152	0.0158

Results are shown in Fig. 2 for the system comprising CO<sub>2</sub> and methane. No appreciable difference is found between the SRK and PR EoSs for all the investigated binary systems.

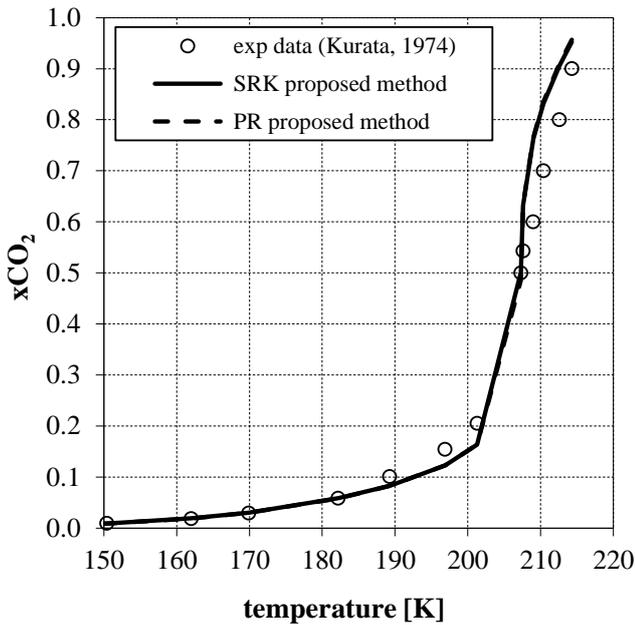


Fig.2, CO<sub>2</sub> freezing points for the CO<sub>2</sub>-methane mixture, obtained experimentally [37] and with the proposed method (SRK and PR EoSs).

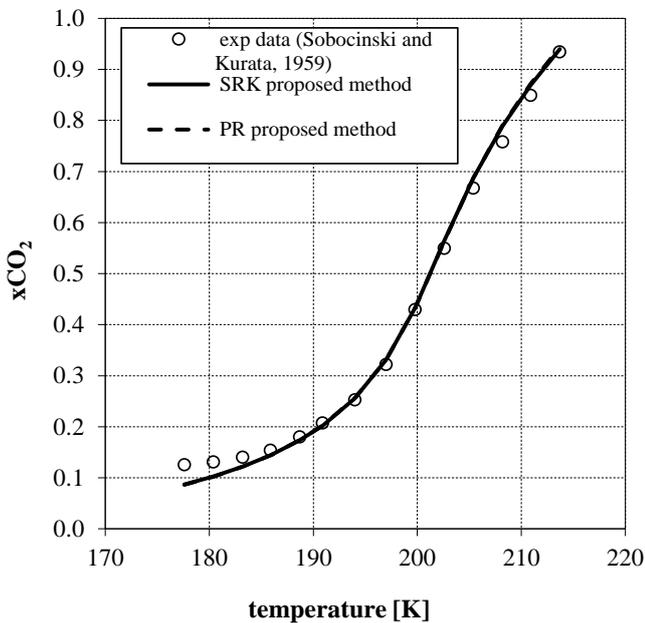


Fig.3, CO<sub>2</sub> freezing points for the CO<sub>2</sub>-H<sub>2</sub>S system, obtained experimentally [35] and with the proposed method (SRK and PR EoSs).

that the proposed method allows a reliable prediction of dry ice formation also in systems containing H<sub>2</sub>S. This is particularly important in cryogenic gas purification processes which aim at reducing the content of acidic components, including H<sub>2</sub>S. In comparison with results reported in [43] for the same system with a different binary interaction parameter, the present results also prove the importance of using optimized  $k_{ij}$ s to achieve phase equilibrium estimations that are in good agreement with experimental evidence. The performances of the proposed method have been also evaluated by comparing the predicted vapor molar fraction of carbon dioxide with the experimental one. A good agreement with experimental data has been obtained as proved by the obtained AAD values for the two EoSs, which are 0.0126 and 0.0049 for SRK and PR EoSs, respectively.

### VI. FREEZING POINTS OF CO<sub>2</sub> IN MULTICOMPONENT MIXTURES

Experimental data of mixtures composed of more than one *n*-alkane and CO<sub>2</sub> have been used to validate the proposed method. Data have been taken from [44]. According to the phase rule, a ternary system has two degrees of freedom to completely fix the solid-liquid-vapor equilibrium state. In addition to the temperature, the liquid molar fraction of the second component in mixture has been chosen as the second variable. In the quaternary system containing carbon dioxide, methane, ethane and propane, the number of degrees of freedom is three. The variables to be specified in addition to the temperature have been the ratio of the liquid molar fraction of methane and ethane and the ratio of the liquid molar fraction of methane and propane. The obtained AAD values are reported in Table 5 and the predicted values of the CO<sub>2</sub> molar fraction in the liquid phase along solid-liquid-vapor locus are reported in Fig. 4 for a comparison with the experimental data for the CO<sub>2</sub>-methane-ethane system. It can be outsourced that the proposed method allows a reliable representation of the SLVE also for multicomponent mixtures, only requiring parameters relevant to CO<sub>2</sub> alone and binary interaction parameters  $k_{ij}$ s.

TABLE 5, AVERAGE ABSOLUTE DEVIATIONS OBTAINED WITH THE PROPOSED METHOD, BOTH WITH SRK EOS AND PR EOS, FOR MULTICOMPONENT MIXTURES

Mixture	AAD SRK EoS	AAD PR EoS
CO <sub>2</sub> -C1-C2	0.0158	0.0167
CO <sub>2</sub> -C1-C3	0.0168	0.0157
CO <sub>2</sub> -C1-C4	0.0251	0.0249
CO <sub>2</sub> -C2-C3	0.0345	0.0341
CO <sub>2</sub> -C1-C2-C3	0.0155	0.0164

The comparison with the experimental data reported by Sobocinski and Kurata [35] is shown in Fig. 3 and suggests

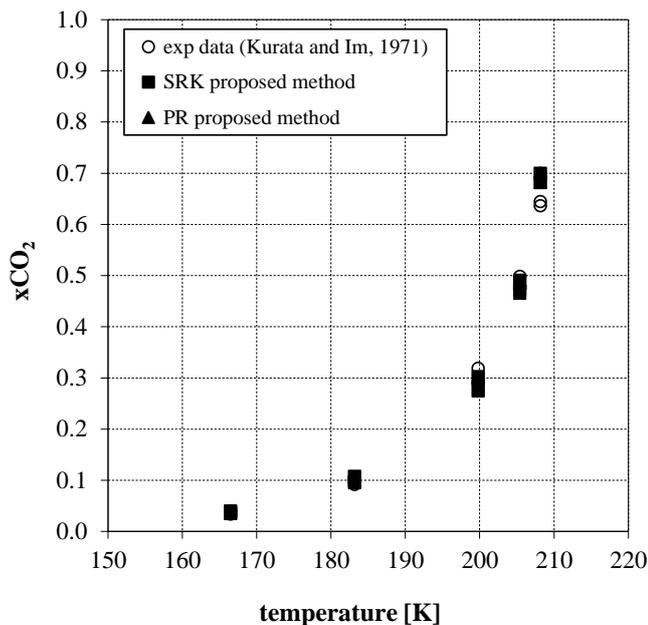


Fig.4, CO<sub>2</sub> freezing points for the CO<sub>2</sub>-C1-C2 system, obtained experimentally [44] and with the proposed method (SRK and PR EoSs).

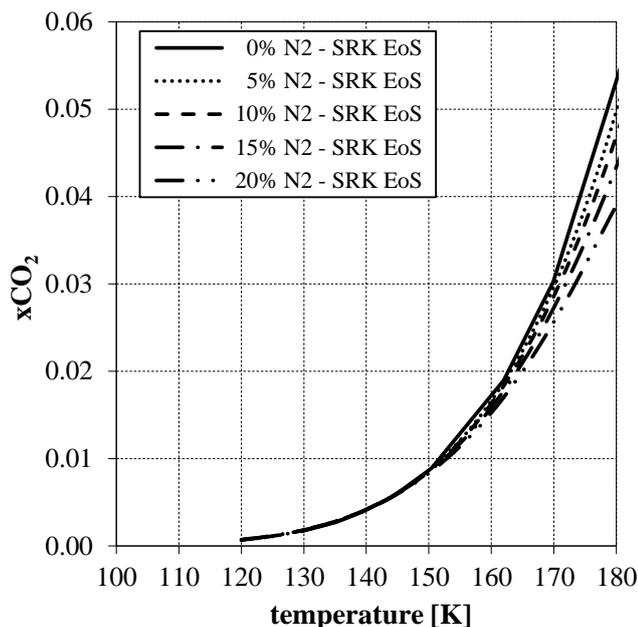


Fig.5, CO<sub>2</sub> freezing points for the CO<sub>2</sub>-N<sub>2</sub>-C1 system, obtained with the proposed method (SRK EoS).

In [43] the effect of the presence of hydrogen sulfide in mixtures containing carbon dioxide and methane is studied and it is shown that the addition of such a component with a higher boiling point than methane increases the solubility of carbon dioxide in the liquid phase.

Likewise, it is interesting to analyze the effect of the presence of nitrogen in a carbon dioxide-methane mixture. Indeed, Lokhandwala et al. [45] have reported that studies performed by the Gas Research Institute reveal that about 14% of known natural gas reserves in the United States are subquality due to a high nitrogen content. Cryogenic processes are among the main technologies used for natural gas denitrogenation. In order to completely define the solid-liquid-vapor equilibrium state of the ternary system comprising CO<sub>2</sub>, nitrogen and methane, the liquid molar fraction of nitrogen has been fixed in addition to the temperature. The nitrogen liquid molar fraction has been varied in the range 5%-20%. The binary interaction parameters for the CO<sub>2</sub>-N<sub>2</sub> pair have been taken from [46]. Fig. 5 shows that the presence of nitrogen does not affect the CO<sub>2</sub> freezing point below a temperature of about 150 K, irrespective of the nitrogen content. On the contrary, at higher temperatures as the amount of nitrogen in mixture increases the CO<sub>2</sub> freeze-out problem is likely to occur at lower CO<sub>2</sub> liquid molar fraction. Although Fig. 5 shows the results obtained by means of SRK EoS, they are similar to those obtained when the PR EoS is used for SLVE calculations. The observed effect due to the presence of nitrogen is in agreement with the results reported by Shen and Lin [16], although they have performed SLE rather than SLVE calculations.

## VII. CONCLUSION

Carbon dioxide freezing points in mixtures containing one or more hydrocarbons and/or non-hydrocarbon compounds should be properly predicted, especially when dealing with cryogenic CO<sub>2</sub> capture to control climate change. In this paper, a thermodynamic method for calculating CO<sub>2</sub> freezing points is presented. It is based on the use of cubic equations of state and of proper adaptive parameters obtained by regression of experimental data of CO<sub>2</sub> sublimation temperature and solid vapor pressure and of CO<sub>2</sub> solubility in binary mixtures. The proposed method has been validated by comparison with experimental data of equilibrium compositions along the solid-liquid-vapor loci of both binary and multicomponent systems. The agreement of the obtained results with experimental data shows the reliability of the proposed method in the representation of solid-liquid-vapor equilibrium calculations. The proposed method has been also used to predict the effect of the addition of nitrogen to CO<sub>2</sub>-methane mixtures. It has been concluded that CO<sub>2</sub> freezing points are slightly affected by the presence of nitrogen in the low-temperature region. On the contrary, as the temperature increases the CO<sub>2</sub> freeze-out problem is more likely to occur for higher nitrogen contents.

## NOMENCLATURE

- $c_p$  = heat capacity at constant pressure
- $f$  = fugacity
- $g$  = molar Gibbs free energy
- $h$  = enthalpy
- $k_{ij}$  = binary interaction parameter between component  $i$  and  $j$
- $P$  = pressure

R = gas constant  
 s = entropy  
 T = temperature  
 T<sub>m</sub> = melting temperature  
 T<sub>i</sub> = triple point temperature  
 x = molar fraction in liquid phase  
 y = molar fraction in vapor phase

*Greek symbols*

γ = activity coefficient  
 Δ = difference  
 φ = fugacity coefficient

*Superscripts*

L = liquid  
 S = solid  
 V = vapor

*Subscripts*

i = component  
 m = melting

*Abbreviations*

AAD = average absolute deviation  
 EoS = equation of state  
 Exp = experimental  
 Npt = number of points  
 PR = Peng-Robinson  
 SRK = Soave-Redlich-Kwong

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