



Calculation of CO₂ 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

Giorgia De Guido*, Stefano Langè, Stefania Moioli and Laura Annamaria Pellegrini

¹Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133 Milano, ITALY

giorgia.deguido@polimi.it

Accepted for publication on 29th November 2014

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 CO₂ can be effectively applied to large point sources, like natural gas production facilities, in order to separate CO₂ from other gaseous products as a concentrated stream which can be readily transported to a storage site. Cryogenic CO₂ 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 CO₂ removal methods can capture CO₂ in a liquid form, making its geological storage relatively easy. Some cryogenic removal technologies are based on the formation of solid CO₂ 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 CO₂ 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 CO₂ 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 CO₂-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, CO₂ 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 CO₂ 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 CO₂ 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 CO₂ in the flue gas is high [4]. They are also of great interest in the natural gas purification industry for the removal of CO₂ 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 CO₂ which can be readily transported by pipeline. Some cryogenic processes can be classified as solid-based CO₂ capture processes. Some examples are CO₂ capture by anti-sublimation [5], the Controlled Freeze ZoneTM technology (CFZTM) [6] and the cryogenic CO₂ 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 C₂-C₅ alkanes [8]. A novel distillation process [9] eliminates solid CO₂ build-up by performing distillation in two columns operated at high and low pressures, respectively. In all these processes the prediction of CO₂ freezing points is key for process design. In the literature it has been reported that unreliable CO₂ 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 CO₂ freezing points.

II. THERMODYNAMIC FRAMEWORK

Some empirical correlations based on CO₂ 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, γ_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 CO₂ and a saturated solution of CO₂ 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 CO₂ 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 CO₂ 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 CO₂ from gaseous streams. Equilibria calculations are based on the equality (Eq. (6)) between the fugacity of CO₂ (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 CO₂ 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 $\Delta g_{L \rightarrow S}(T, P)$ for pure CO₂ 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).

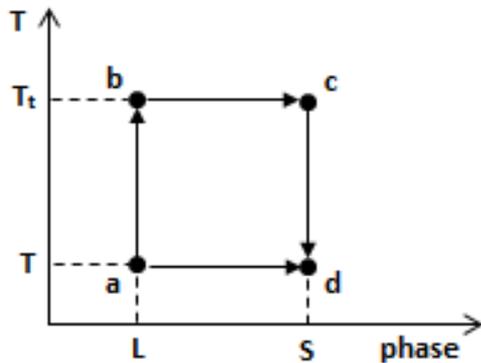


Fig.1, Thermodynamic cycle for the derivation of an expression for the ratio $f_i^S(T,P)/f_i^L(T,P)$.

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 CO₂ 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 CO₂ 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 CO₂ in the solid phase strongly depends on its heat of fusion, Δh_m , on the difference between its liquid and solid heat capacities and on its melting temperature, T_m . 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_{ijS} (Table 2) for both SRK and PR EoSs have been obtained by regression of experimental solubility data of binary mixtures containing CO₂ and *n*-alkanes at low temperatures [37]. Also the value of the binary interaction parameters for the CO₂-H₂S pair has been optimized by regression of experimental data [35] of vapor and liquid composition along V-L-CO_{2, solid} 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 ₂ -C1	0.1243	0.1230
CO ₂ -C2	0.1332	0.1281
CO ₂ -C3	0.1235	0.1185
CO ₂ -C4	0.1150	0.1109
CO ₂ -C5	0.1067	0.1007
CO ₂ -C6	0.1021	0.0991
CO ₂ -H ₂ S	0.1020	0.0992

In this work k_{ijS} for hydrocarbon-hydrocarbon pairs have been taken from ASPEN HYSYS® [38], as well as those for the H₂S-hydrocarbon pairs and for the N₂-CH₄ pair. They are reported in Table 3. It is worth noticing that k_{ijS} 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 ₂ S	0.0888	0.0850
C1-N ₂	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 ₂ 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 ₂ S	0.0925	0.0750
C4-C5	0.0005	0.0005
C4-C6	0.0019	0.0019
C4-H ₂ S	0.0626	0.0600
C5-C6	0.0004	0.0004
C5-H ₂ S	0.0709	0.0650
C6-H ₂ S	0.0570	0.0600

V. FREEZING POINTS OF CO₂ IN BINARY MIXTURES

The composition of the liquid phase along solid-liquid-vapor locus of binary mixtures containing CO₂ 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 ₂ -C1	0.0374	0.0391
CO ₂ -C2	0.0122	0.0118
CO ₂ -C3	0.0274	0.0259
CO ₂ -C4	0.0340	0.0316
CO ₂ -C5	0.0543	0.0537
CO ₂ -C6	0.0706	0.0698
CO ₂ -H ₂ S	0.0152	0.0158

Results are shown in Fig. 2 for the system comprising CO₂ and methane. No appreciable difference is found between the SRK and PR EoSs for all the investigated binary systems.

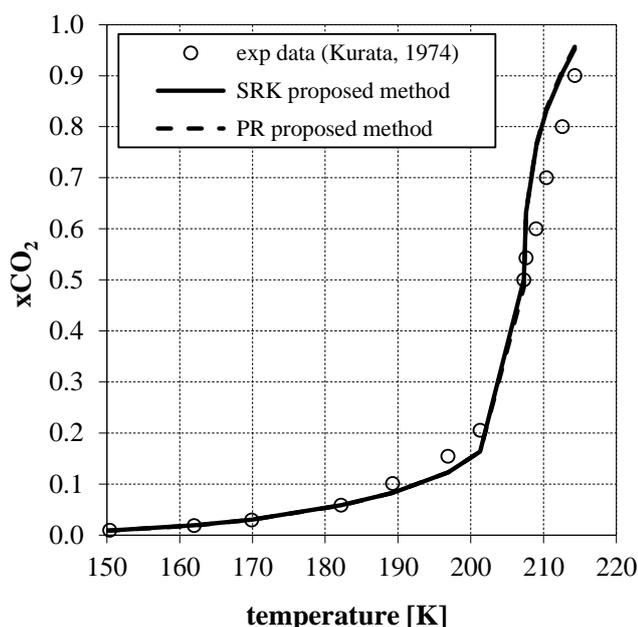


Fig.2, CO₂ freezing points for the CO₂-methane mixture, obtained experimentally [37] and with the proposed method (SRK and PR EoSs).

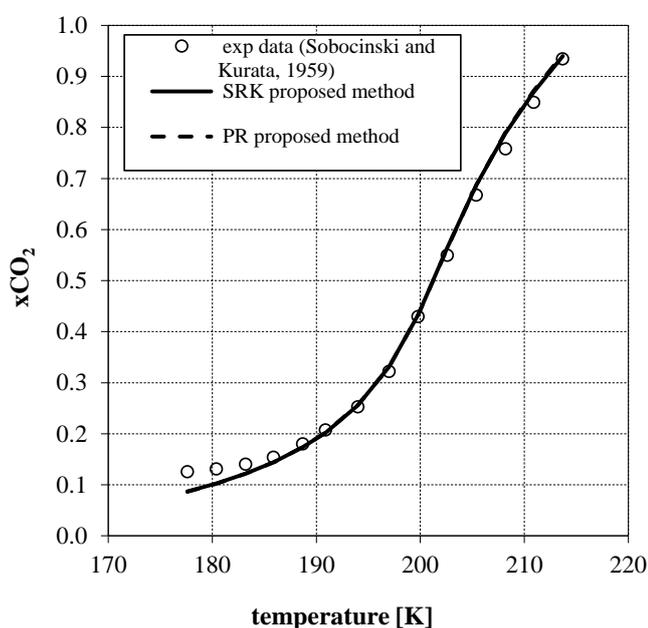


Fig.3, CO₂ freezing points for the CO₂-H₂S system, obtained experimentally [35] and with the proposed method (SRK and PR EoSs).

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

that the proposed method allows a reliable prediction of dry ice formation also in systems containing H₂S. This is particularly important in cryogenic gas purification processes which aim at reducing the content of acidic components, including H₂S. 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 CO₂ IN MULTICOMPONENT MIXTURES

Experimental data of mixtures composed of more than one n -alkane and CO₂ 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 CO₂ 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 CO₂-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 CO₂ 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 ₂ -C1-C2	0.0158	0.0167
CO ₂ -C1-C3	0.0168	0.0157
CO ₂ -C1-C4	0.0251	0.0249
CO ₂ -C2-C3	0.0345	0.0341
CO ₂ -C1-C2-C3	0.0155	0.0164

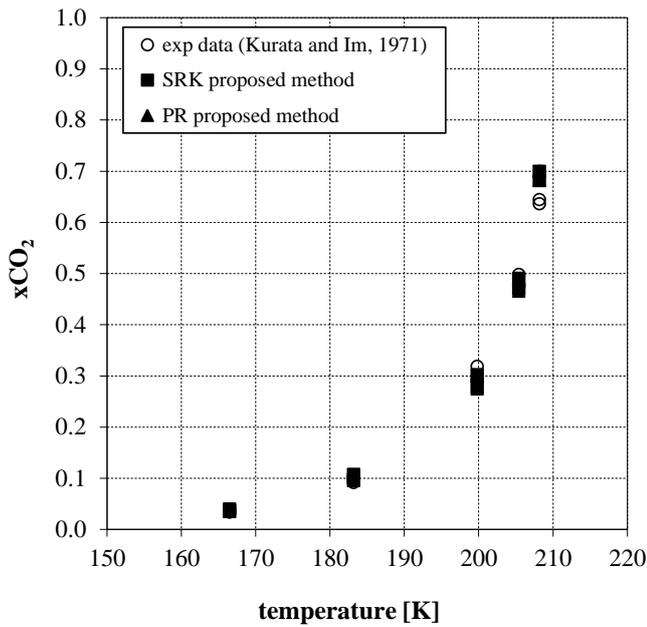


Fig.4, CO₂ freezing points for the CO₂-C1-C2 system, obtained experimentally [44] and with the proposed method (SRK and PR EoSs).

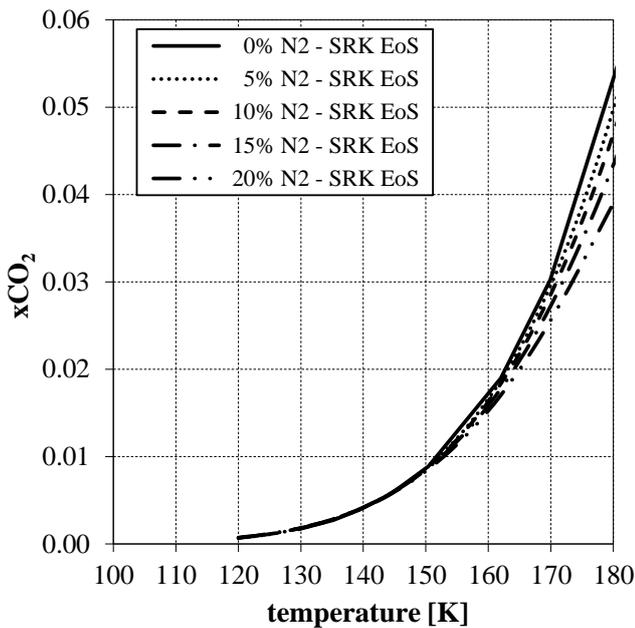


Fig.5, CO₂ freezing points for the CO₂-N₂-C1 system, obtained with the proposed method (SRK EoS).

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 CO₂, 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 CO₂-N₂ pair have been taken from [46]. Fig. 5 shows that the presence of nitrogen does not affect the CO₂ 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 CO₂ freeze-out problem is likely to occur at lower CO₂ 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 CO₂ capture to control climate change. In this paper, a thermodynamic method for calculating CO₂ 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 CO₂ sublimation temperature and solid vapor pressure and of CO₂ 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 CO₂-methane mixtures. It has been concluded that CO₂ freezing points are slightly affected by the presence of nitrogen in the low-temperature region. On the contrary, as the temperature increases the CO₂ 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_m = melting temperature
 T_i = 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

REFERENCES

- [1] O. Edenhofer, R. Pichs-Madruga, Y. Sokona, E. Farahani, S. Kadner, K. Seyboth, A. Adler, I. Baum, S. Brunner, P. Eickemeier, B. Kriemann, J. Savolainen, S. Schlömer, C. von Stechow, T. Zwickel and J.C. Minx, "Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change," 2014.
- [2] A. B. Rao and E. S. Rubin, "A Technical, Economic, and Environmental Assessment of Amine-Based CO₂ Capture Technology for Power Plant Greenhouse Gas Control," *Environmental Science & Technology*, vol. 36, pp. 4467-4475, 2002.
- [3] M. J. Tuinier, et al., "Cryogenic capture using dynamically operated packed beds," *Chemical Engineering Science*, vol. 65, pp. 114-119, 2010.
- [4] P. Riemer, "Greenhouse gas mitigation technologies, an overview of the CO₂ capture, storage and future activities of the IEA Greenhouse Gas R&D programme," *Energy Conversion and Management*, vol. 37, pp. 665-670, 1996.
- [5] D. Clodic and M. Younes, "CO₂ capture by anti-sublimation Thermo-economic process evaluation," in *Fourth Annual Conference on Carbon Capture & Sequestration*, Alexandria, USA, 2005.
- [6] B. T. Kelley, et al., "Controlled Freeze Zone™ for developing sour gas reserves," *Energy Procedia*, vol. 4, pp. 824-829, 2011.
- [7] S. Burt, et al., "Cryogenic CO₂ Capture to Control Climate Change Emissions," in *The 34th International Technical Conference on Clean Coal & Fuel Systems May*, 2009.
- [8] A. S. Holmes and J. M. Ryan, "Cryogenic distillative separation of acid gases from methane," US 4318723 United States Mon Dec 14 09:26:01 EST 2009 EDB-84-183118 English, 1982.
- [9] L. A. Pellegrini, "Process for the removal of CO₂ from acid gas," ed: Google Patents, 2014.
- [10] T. Eggeman and S. Chafin, "Pitfalls of CO₂ freezing prediction," in *82nd Annual Convention of the GPA. San Antonio, USA: GPA*, 2003.
- [11] B. ZareNezhad and T. Eggeman, "Application of Peng-Robinson equation of state for CO₂ freezing prediction of hydrocarbon mixtures at cryogenic conditions of gas plants," *Cryogenics*, vol. 46, pp. 840-845, 2006.
- [12] A. Myers and J. Prausnitz, "Thermodynamics of solid carbon dioxide solubility in liquid solvents at low temperatures," *Industrial & Engineering Chemistry Fundamentals*, vol. 4, pp. 209-212, 1965.
- [13] J. Hildebrand and R. Scott, "The Solubility of Nonelectrolytes, Reinhold Publ," *Corp, New York*, 1950.
- [14] G. Preston and J. Prausnitz, "Thermodynamics of solid solubility in cryogenic solvents," *Industrial & Engineering Chemistry Process Design and Development*, vol. 9, pp. 264-271, 1970.
- [15] D. J. Dixon and K. P. Johnston, "Molecular thermodynamics of solubilities in gas antisolvent crystallization," *AIChE Journal*, vol. 37, pp. 1441-1449, 1991.
- [16] T. Shen and W. Lin, "Calculation of Carbon Dioxide Solubility in Liquefied Natural Gas," *Int. J. Chem. Eng. Appl*, vol. 2, pp. 366-371, 2011.
- [17] J. G. Gmehling, et al., "Solid-liquid equilibria using UNIFAC," *Industrial & Engineering Chemistry Fundamentals*, vol. 17, pp. 269-273, 1978.
- [18] T. Eggeman and S. Chafin, "Beware the pitfalls of CO₂ freezing prediction," *Chemical Engineering Progress*, vol. 101, pp. 39-44, 2005.
- [19] V. Feroiu, et al., "Modelling the Solubility of Solid Aromatic Compounds in Supercritical Fluids," *REVISTA DE CHIMIE*, vol. 61, pp. 685-690, 2010.
- [20] G. Xu, et al., "Reliable computation of high-pressure solid-fluid equilibrium," *Industrial & Engineering Chemistry Research*, vol. 39, pp. 1624-1636, 2000.

- [21] M. Yazdizadeh, et al., "Thermodynamic modeling of solubilities of various solid compounds in supercritical carbon dioxide: Effects of equations of state and mixing rules," *The Journal of Supercritical Fluids*, vol. 55, pp. 861-875, 2011.
- [22] M. Yazdizadeh, et al., "Applications of cubic equations of state for determination of the solubilities of industrial solid compounds in supercritical carbon dioxide: A comparative study," *Chemical Engineering Science*, vol. 71, pp. 283-299, 2012.
- [23] I. Kikic, et al., "A thermodynamic analysis of three-phase equilibria in binary and ternary systems for applications in rapid expansion of a supercritical solution (RESS), particles from gas-saturated solutions (PGSS), and supercritical antisolvent (SAS)," *Industrial & Engineering Chemistry Research*, vol. 36, pp. 5507-5515, 1997.
- [24] M. Seiler, et al., "Modeling of solid/fluid phase equilibria in multicomponent systems at high pressure," *Chemical Engineering & Technology*, vol. 24, pp. 607-612, 2001.
- [25] X. Tang and J. Gross, "Modeling the phase equilibria of hydrogen sulfide and carbon dioxide in mixture with hydrocarbons and water using the PCP-SAFT equation of state," *Fluid Phase Equilibria*, vol. 293, pp. 11-21, 2010.
- [26] G. Soave, "Equilibrium constants from a modified Redlich-Kwong equation of state," *Chemical Engineering Science*, vol. 27, pp. 1197-1203, 1972.
- [27] D.-Y. Peng and D. B. Robinson, "A new two-constant equation of state," *Industrial & Engineering Chemistry Fundamentals*, vol. 15, pp. 59-64, 1976.
- [28] J. M. Prausnitz, et al., *Molecular thermodynamics of fluid-phase equilibria*: Pearson Education, 1998.
- [29] G. S. Soave, "Application of the redlich-kwong-soave equation of state to solid-liquid equilibria calculations," *Chemical Engineering Science*, vol. 34, pp. 225-229, 1979.
- [30] W. Giauque and C. Egan, "Carbon dioxide. The heat capacity and vapor pressure of the solid. The heat of sublimation. Thermodynamic and spectroscopic values of the entropy," *The Journal of Chemical Physics*, vol. 5, pp. 45-54, 2004.
- [31] G. W. C. Kaye and T. H. Laby, *Tables of physical and chemical constants: and some mathematical functions*: Longmans, Green and co., 1921.
- [32] D. R. Stull, "Vapor pressure of pure substances. Organic and inorganic compounds," *Industrial & Engineering Chemistry*, vol. 39, pp. 517-540, 1947.
- [33] T. Tables, "Selected values of properties of chemical compounds," *Thermodynamic Research Center Data Project, Texas A&M University, College Station*, vol. 971, pp. 2605-2609, 1974.
- [34] AspenTech, *ASPEN Properties Databank*[®]. Burlington, MA: AspenTech, 2010.
- [35] D. Sobocinski and F. Kurata, "Heterogeneous phase equilibria of the hydrogen sulfide-carbon dioxide system," *AIChE Journal*, vol. 5, pp. 545-551, 1959.
- [36] M. Zabransky, et al., "Heat capacity, melting enthalpies, and melting temperatures of pure liquid inorganic compounds," *Chem. Prum*, vol. 38, pp. 67-73, 1988.
- [37] F. Kurata, *Solubility of solid carbon dioxide in pure light hydrocarbons and mixtures of light hydrocarbons*: Gas Processors Association, 1974.
- [38] AspenTech, *Aspen HYSYS*[®]. Burlington, MA: AspenTech, 2010.
- [39] J. Brewer and F. Kurata, "Freezing points of binary mixtures of methane," *AIChE Journal*, vol. 4, pp. 317-318, 1958.
- [40] J. Davis, et al., "Solid-liquid-vapor phase behavior of the methane-carbon dioxide system," *AIChE Journal*, vol. 8, pp. 537-539, 1962.
- [41] R. H. Jensen and F. Kurata, "Heterogeneous phase behavior of solid carbon dioxide in light hydrocarbons at cryogenic temperatures," *AIChE Journal*, vol. 17, pp. 357-364, 1971.
- [42] U. K. Im, *Solubility of Solid Carbon Dioxide in Certain Paraffinic Hydrocarbons: Binary, Ternary and Quaternary Systems*: University of Kansas, 1970.
- [43] G. De Guido, et al., "Thermodynamic method for the prediction of solid CO₂ formation from multicomponent mixtures," *Process Safety and Environmental Protection*, vol. 92, pp. 70-79, 2014.
- [44] F. Kurata and K. U. Im, "Phase equilibrium of carbon dioxide and light paraffins in presence of solid carbon dioxide," *Journal of Chemical & Engineering Data*, vol. 16, pp. 295-299, 1971.
- [45] K. A. Lokhandwala, et al., "Nitrogen removal from natural gas using membranes," in *Proceedings of the Natural Gas Conference, Federal Energy Technology Center (FETC), Houston, Texas, March*, 1999.
- [46] L. A. Pellegrini, et al., "Prediction of vapor-liquid equilibrium for reservoir mixtures with cubic equations of state: Binary interaction parameters for acidic gases," *Fluid Phase Equilibria*, vol. 326, pp. 45-49, 2012.