

Thermodynamic method for the prediction of solid CO₂ formation from multicomponent mixtures

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1. Introduction

The global energy demand is expected to grow rapidly over the next twenty years, even if the population growth rate is decreasing. In this scenario, by 2030 natural gas is projected to meet 31% of the global energy demand with its main applications in power plants (about 38%) and in the industrial sector (about 60%) (BP, 2012). The increase of both the energy and gas demand has led energy companies to find out solutions to satisfy the request.

Nowadays the attention is focused also on those gas fields that were considered to be not suitable for market purposes in the past, due to the high impurities contained and to the low gas quality (Langè et al., 2013; Pellegrini et al., 2013). Thus, industries are developing new strategies to allow the

exploitation of these reservoirs that have been estimated to be approximately 40% of natural gas reservoirs (Foster and Carroll, 2008). When the content of CO₂ and H₂S becomes higher, traditional solutions for gas purification (chemical and physical absorption) (Moioli et al., 2013) may not be economically sustainable to be used. Under this scenario, the upgrading of natural gas through cryogenic distillation or separation based on solidification is preferred to traditional purification techniques (Pires et al., 2011). Cryogenic processes can be also applied for CO₂ post-combustion capture from power plant flue gases (Khoo and Tan, 2006; Tuinier et al., 2010).

In the natural gas production, the state-of-the-art technologies for cryogenic upgrading are the Ryan–Holmes process (Holmes et al., 1983; Holmes and Ryan, 1982a,b) and the

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Controlled-Freeze-Zone process by Exxon Mobil (Haut et al., 1989; Michael E. Parker et al., 2011; Northrop and Valencia, 2009; Valencia and Denton, 1985; Valencia and Victory, 1990). The former uses a third component as entrainer (typically a light hydrocarbon) to avoid CO₂ solidification, while the latter allows the formation of solid carbon dioxide and confines it to a particular zone of the column, with the subsequent melting of dry ice over a specifically designed tray (Valencia and Victory, 1993). For the cryogenic CO₂ removal from exhaust gases of power plants, Tuinier et al. (2010) have proposed a method which separates CO₂ and water on the basis of differences in dew and sublimation points, using dynamically operated packed beds.

During the operation of cryogenic processes in which CO₂ precipitation has to be avoided, the CO₂ freeze-out problem arises and must be solved to prevent equipment blockage, plugging, ruptures and failure, with risks related to the safety aspects of handling cryogenic liquids and solids. The plugging problems caused by dry ice formation are similar to the ones related to gas hydrates in natural gas extraction wells. The cryogenic temperatures cause stresses in the pipe: the combination of these with other residual stresses, the expansion of the solid and the defects already present in the construction material can threaten the integrity of the pipe (Bowen et al., 1996). Moreover, dry ice plug generates high pressure behind the block. When the pressure beyond the dry ice cap decreases, the solid block is ejected due to the high pressure difference and pipe or hose ruptures occurs, particularly when curves are present along the route of the pipeline (AIGA, 2009).

Dry ice can also trap the gas near the inner pipe wall; if excess heat is given to that zone, the gas pressure will increase, causing possible fractures in the pipe.

Attention must be devoted also to the rapid depressurization of gaseous streams containing high quantities of carbon dioxide at lower temperatures (pressure drops or Joule–Thomson valves). Under these conditions, a liquid phase may form and, if the CO₂ content inside the liquid is high, precipitation of the solid may occur, with subsequent damages if the solid plug is formed in the line or if the solid is transported to a vessel (AIGA, 2009).

Carbon dioxide freezing calculations are also involved in the design of other unit operations, such as heat exchangers, equipment fittings and turboexpanders used in demethanizer columns (Eggeman and Chafin, 2005; Le and Trebble, 2007).

The major safety issue concerning this possible equipment rupture and subsequent cryogenic fluid release is that, when the problem occurs in natural gas cryogenic processing plants, the liquid spill can be followed by a violent vaporization, leading to the formation of a vapor cloud with the risk of accidental fire or explosion (Sklavounos and Rigas, 2005). Moreover, the formation of solid carbon dioxide produces static electricity (AIGA, 2009), so its presence inside combustible atmospheres (accidental releases) can be a potential source of fire risk.

For plant operators, exposure to cryogenic solids or fluids can cause frost burns (Bowen et al., 1996) and damages to eyes and skin such as corneal burns and deep-freezing of the tissues (AIGA, 2009). When the cryogenic fluid and dry ice are released into the atmosphere, the level of oxygen in the nearby ambient is decreased, with risks of asphyxia (Bowen et al., 1996). Since CO₂ is a slightly acid, when its concentration becomes particularly high, if inhaled, it can change the normal pH of blood, with harmful toxic effects on humans such as severe and disruptive acidosis tissues (AIGA, 2009).

Thus, in chemical process design the prediction of the solubility of solids in liquids is of great interest, especially when process conditions may lead to the precipitation of a solid. As reported in literature (Eggeman and Chafin, 2003), “process simulators are not reliably matching data for even simple systems”, such as the mixture composed of methane and CO₂. As a result, reliable thermodynamic tools are required for accurately predicting CO₂ freezing solubility in hydrocarbon mixtures.

2. Thermodynamic framework

2.1. State of the art

For the thermodynamic modeling of the solubility of a solid in a liquid solvent (i.e., the thermodynamics of solid–liquid equilibria or SLE) or at the triple point in a mixture (i.e., the thermodynamics of solid–liquid–vapor equilibria or SLVE), the starting point is equating the partial fugacity for each component in each phase:

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

$$f_i^S(T, P) = \hat{f}_i^V(T, P, \underline{y}) \quad (1b)$$

$$\hat{f}_i^L(T, P, \underline{x}) = \hat{f}_i^V(T, P, \underline{y}) \quad (1c)$$

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, at the system temperature and pressure. Some authors (Bergman and Yarborough, 1978; White et al., 1973) have developed empirical correlations based on CO₂ freeze-out experiments. However, the experience has shown that these correlations are not trustable enough to be used for industrial applications. Thus, to solve the problem, two thermodynamic approaches are typically used: the activity coefficient model and the Equation of State (EoS) model. The activity coefficient approach has been used by Myers and Prausnitz (1965), who relate the activity coefficient of carbon dioxide in the liquid solvent to pertinent intermolecular forces by a generalization of Scatchard’s equation. Also Preston and Prausnitz (1970) estimate the solubility of solids in cryogenic liquid solvents by means of the activity coefficient approach, with the activity coefficients calculated from Scatchard’s equation with a correction to Hildebrand’s geometric mean assumption for cohesive energy density. The activity coefficients which have to be calculated when the activity coefficient approach is selected for predicting the solubility of solutes in non-electrolyte liquid mixtures can be also estimated from the group-contribution method UNIFAC (Gmehling et al., 1978) or from the Non-Random Two Liquid (NRTL) equation (Eggeman and Chafin, 2005).

The other approach found in literature is based on the use of an Equation of State (EoS) for equilibrium calculations involving the solid phase. Eggeman and Chafin (2005), ZareNezhad and Eggeman (2006) and Shen and Lin (2011) all report the same equation to describe the solubility of carbon dioxide in liquid hydrocarbons. Although, according to Eggeman and Chafin (2005) and ZareNezhad and Eggeman (2006), any EoS can be used to calculate the required fugacity coefficients, the mentioned authors choose a standard form of the PR equation, which is widely used to model natural gas processing systems. On the other hand, Shen and Lin (2011) select the PR and the SRK equations for SLE calculations. An

expression similar to that presented by [Eggeman and Chafin \(2005\)](#), [ZareNezhad and Eggeman \(2006\)](#) and [Shen and Lin \(2011\)](#) can be also found in works by other authors ([Feroiu et al., 2010](#); [Xu et al., 2000](#); [Yazdizadeh et al., 2011, 2012](#)) who, however, deal with the solubility of solid compounds in a supercritical fluid. An EoS approach is also used by [Kikic et al. \(1997\)](#), who compute the fugacity coefficient of the solute in the liquid (or fluid) phase by means of the PR EoS.

Also [Tang and Gross \(2010\)](#) choose an EoS approach for solid–fluid equilibria calculations, since they decide to describe the non-ideality of the fluid phases by an EoS. In the expression they propose for the solubility of the solute in the fluid phase, which is also reported by [Seiler et al. \(2001\)](#), the fugacity coefficient is calculated from the perturbed-chain polar statistical associating fluid theory (PCP-SAFT) EoS.

A mixed approach is reported by [Dixon and Johnston \(1991\)](#), who investigate a predictive molecular thermodynamic model of the solubility of solids in liquids expanded with gaseous CO₂; to do that, they combine an expanded liquid EoS approach with Scatchard’s regular solution theory ([Prausnitz et al., 1986](#)).

In this work, cubic Equations of State with proper adaptive parameters, typical of the SLV equilibrium, have been applied to predict solubility of solid CO₂ in systems containing compounds of interest mainly in natural gas purification units. Particular attention has been devoted to obtain an accurate description of the solubility curve for CO₂ binary as well as multicomponent mixtures.

2.2. Proposed method

The proposed method is based on a ϕ/ϕ approach: the solid–liquid–vapor equilibrium is described by setting, according to Eq. (1a), the fugacity of the component in the solid phase, considered as a pure solute, equal to the one in the liquid phase calculated at the system temperature and bubble pressure, where fugacity coefficients are obtained by means of an EoS. In this work, the Soave–Redlich–Kwong (SRK) ([Soave, 1972](#)) and the Peng–Robinson (PR) ([Peng and Robinson, 1976](#)) EoSs have been used.

Most of the component properties and of the binary interaction parameters of pairs other than those involving carbon dioxide have been taken from ASPEN HYSYS® ([AspenTech, 2010a](#)).

Considering the EoS approach, in order to perform solid–liquid–vapor equilibria calculations, the isofugacity relation for CO₂ can be written as:

$$f_{\text{CO}_2}^{\text{S}}(T, P) = \hat{f}_{\text{CO}_2}^{\text{L}}(T, P, \underline{x}) = P \cdot x_{\text{CO}_2} \cdot \hat{\phi}_{\text{CO}_2}^{\text{L}}(T, P, \underline{x}) \quad (2)$$

where P is the bubble pressure calculated according to Eq. (1c), since a three-phase (SLV) equilibrium is considered.

The description of such equilibria can be done by considering the rigorous thermodynamic relation which allows to express the fugacity of a pure component in the solid state as a function of that in the liquid state, at the same temperature and pressure. Fig. 1 shows the thermodynamic cycle which has been used to obtain the ratio between $f_{\text{CO}_2}^{\text{L}}(T, P)$ and $f_{\text{CO}_2}^{\text{S}}(T, P)$ ([Gmehling et al., 2012](#)).

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 bubble pressure and by substituting the chemical potential of the pure component with the molar Gibbs free energy, $\Delta g_{a \rightarrow d}(T, P)$ can also be

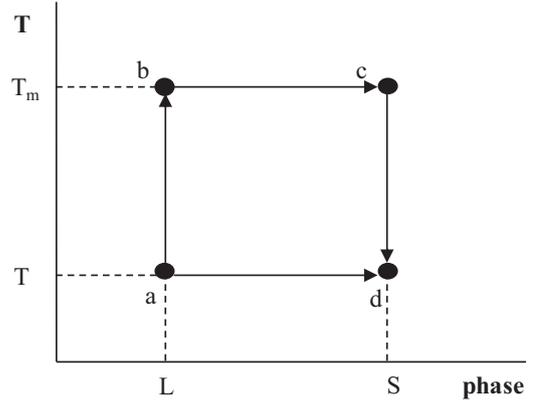


Fig. 1 – Thermodynamic cycle for the derivation of an expression for the ratio $f_i^{\text{S}}(T, P)/f_i^{\text{L}}(T, P)$.

obtained from the enthalpy and entropy changes of the same step $a \rightarrow d$ shown in Fig. 1:

$$RT \ln \frac{f_{\text{CO}_2}^{\text{S}}(T, P)}{f_{\text{CO}_2}^{\text{L}}(T, P)} = \Delta g_{a \rightarrow d}(T, P) = \Delta h_{a \rightarrow d}(T, P) - T \Delta s_{a \rightarrow d}(T, P) \quad (3)$$

Since both the enthalpy and the 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 $\Delta g_{a \rightarrow d}(T, P)$ can be calculated following the path $a \rightarrow b \rightarrow c \rightarrow d$:

$$\begin{aligned} \Delta h_{\text{sol}}(T, P) &= \Delta h_{a \rightarrow d} = \Delta h_{a \rightarrow b} + \Delta h_{b \rightarrow c} + \Delta h_{c \rightarrow d} \\ &= \int_T^{T_m} c_p^{\text{L}}(T) dT - \Delta h_m(T_m) + \int_{T_m}^T c_p^{\text{S}}(T) dT \\ &= \int_T^{T_m} [c_p^{\text{L}}(T) - c_p^{\text{S}}(T)] dT - \Delta h_m(T_m) \end{aligned} \quad (4)$$

$$\begin{aligned} \Delta s_{\text{sol}}(T, P) &= \Delta s_{a \rightarrow d} = \Delta s_{a \rightarrow b} + \Delta s_{b \rightarrow c} + \Delta s_{c \rightarrow d} \\ &= \int_T^{T_m} \frac{c_p^{\text{L}}(T)}{T} dT - \frac{\Delta h_m(T_m)}{T_m} + \int_{T_m}^T \frac{c_p^{\text{S}}(T)}{T} dT \\ &= \int_T^{T_m} \frac{c_p^{\text{L}}(T) - c_p^{\text{S}}(T)}{T} dT - \frac{\Delta h_m(T_m)}{T_m} \end{aligned} \quad (5)$$

Assuming a constant value for the difference of liquid and solid heat capacities, the ratio of the fugacities of CO₂ in the solid and liquid phase is expressed according to:

$$\ln \frac{f_{\text{CO}_2}^{\text{S}}(T, P)}{f_{\text{CO}_2}^{\text{L}}(T, P)} = \frac{\Delta h_m}{RT_m} \left(1 - \frac{T_m}{T}\right) + \frac{\Delta c_p(T_m - T)}{RT} - \frac{\Delta c_p}{R} \ln \frac{T_m}{T} \quad (6)$$

The previous equation can be combined with Eq. (2), leading to the final result for the solubility of CO₂ in a mixture at the triple point:

$$x_{\text{CO}_2} = \frac{\hat{\phi}_{\text{CO}_2}^{\text{L}}(T, P) \cdot \exp \left[\frac{\Delta h_m}{RT_m} \left(1 - \frac{T_m}{T}\right) + \frac{\Delta c_p}{R} \left(\frac{T_m}{T} - 1 - \ln \frac{T_m}{T}\right) \right]}{\hat{\phi}_{\text{CO}_2}^{\text{L}}(T, P, \underline{x})} \quad (7)$$

Table 1 – Parameters involving properties of the solid phase.

Parameters	SRK EoS	PR EoS	Exp.	Source
$\Delta h_m/R/T_m$	4.5769	4.6774	4.6266	Zabransky et al. (1988)
$\Delta c_p/R$	1.4792	0.9179	1.7145	Aspen Properties Databank, AspenTech, 2010b
T_m (K)	216.39	216.16	216.59	Sobocinski and Kurata, 1959

3. Adaptive parameters

3.1. Parameters involving properties of the solid phase

As shown in Section 2.2, the description of the solid phase fugacity is strongly dependent on the heat of fusion Δh_m , on the specific heat of the liquid $c_p^L(T)$ and of the solid $c_p^S(T)$ phases and on the fusion temperature T_m of the freezing compound, in the specific case carbon dioxide. Proper values of these physical quantities have been assumed as adaptive parameters and have been determined to well reproduce the available experimental data. For this reason, their value depends on the used EoS.

In this work a regression of $\frac{\Delta h_m}{RT_m}$, $\frac{\Delta c_p}{R}$ and T_m for carbon dioxide has been performed on the basis of experimental data of sublimation temperature and solid vapor pressure (Giauque and Egan, 1937; Kaye and Laby, 1973; Stull, 1947; TRC, 1980).

The regressed parameters have been obtained by minimizing, using the Newton method, the objective function:

$$f_{ob} = \sum_{j=1}^{npt} err_j^2 \quad (8)$$

where npt is the number of points considered and err_j is calculated as:

$$err_j = \ln f_{CO_2}^S(T_j, P_j) - \ln f_{CO_2}^L(T_j, P_j) - \left[\frac{\Delta h_m}{RT_m} \left(1 - \frac{T_m}{T_j} \right) + \frac{\Delta c_p(T_m - T_j)}{RT_j} - \frac{\Delta c_p}{R} \ln \frac{T_m}{T_j} \right] \quad (9)$$

The obtained values are reported in Table 1, along with experimental data (AspenTech, 2010b; Sobocinski and Kurata, 1959; Zabransky et al., 1988) for a comparison aimed at verifying the physical congruity of the proposed method. A very good agreement can be achieved for T_m and $\frac{\Delta h_m}{RT_m}$, whereas quite a higher discrepancy has been found for $\frac{\Delta c_p}{R}$. This result may be due to a lack of experimental values of the difference between the specific heat for the liquid and of the solid phases. In our opinion, however, the obtained values can be considered physically consistent and have been used in the following.

Table 2 – Optimized values of binary interaction parameters obtained in the proposed method for SRK and PR.

Mixture	SRK EoS	PR EoS
CO ₂ -C1	0.1243	0.1229
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

Table 3 – Values of binary interaction parameters taken from ASPEN HYSYS® (AspenTech, 2010a) 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
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	0.0006
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	N/A
C6-H ₂ S	0.0570	0.0600

3.2. Binary interaction parameters

Generally, proper values of binary interaction parameters are fundamental for a reliable description of the thermodynamic behavior of a system. These parameters are involved in the calculation of the fugacity of a species in a mixture, which influences the obtained solubility results.

New values (Table 2) of k_{ij} for both SRK and PR have been used in the proposed method, to take into account also the presence of the solid phase. They have been obtained by regression of experimental solubility data of binary mixtures containing CO₂ and *n*-alkanes at cryogenic conditions. From the results shown in Section 4 it can be outsourced that these new values of k_{ij} derived from solubility data of CO₂ in pure solvents give also good results for multicomponent systems. The value of the binary interaction parameters for the CO₂-H₂S pair has been taken from Pellegrini et al. (2012), where its value was optimized for the vapor-liquid equilibrium, because of the lacking of solubility experimental data for this pair of compounds. Since the considered *n*-alkanes belong to an

Table 4 – Average absolute deviations obtained with the proposed method, both with SRK and with PR, for binary mixtures.

Mixture	AAD SRK	AAD PR
CO ₂ -methane	0.0471	0.0487
CO ₂ -ethane	0.0115	0.0111
CO ₂ -propane	0.0248	0.0259
CO ₂ - <i>n</i> -butane	0.0374	0.0348
CO ₂ - <i>n</i> -pentane	0.0543	0.0537
CO ₂ - <i>n</i> -hexane	0.0714	0.0713

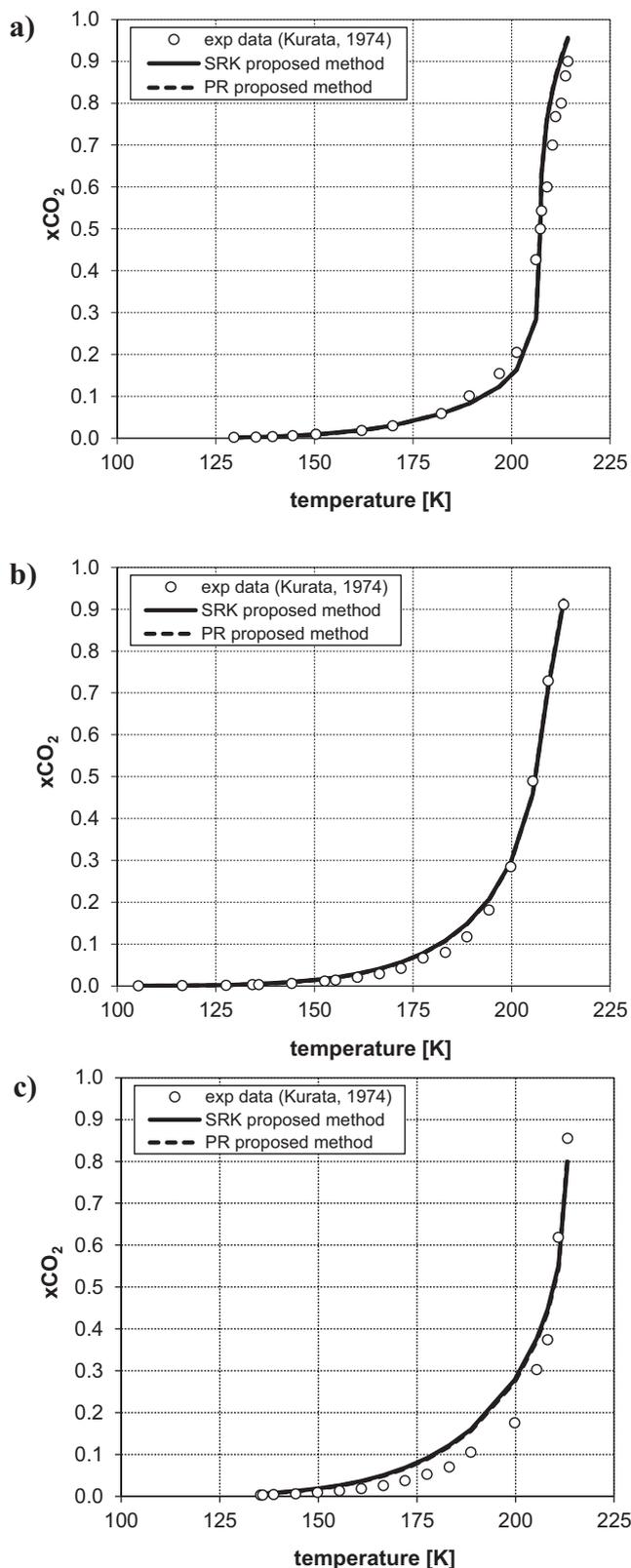


Fig. 2 – Solubility of solid CO₂ in liquid (a) methane, (b) ethane and (c) n-butane, obtained experimentally (Kurata, 1974) and with the proposed method (SRK and PR).

homologous series of related apolar compounds with a similar molecular weight and chemical structure, interactions between two of them are not significant. Although in literature the k_{ij} for the hydrocarbon–hydrocarbon pairs are assumed to be zero (Soave, 1979), in this work they have been taken

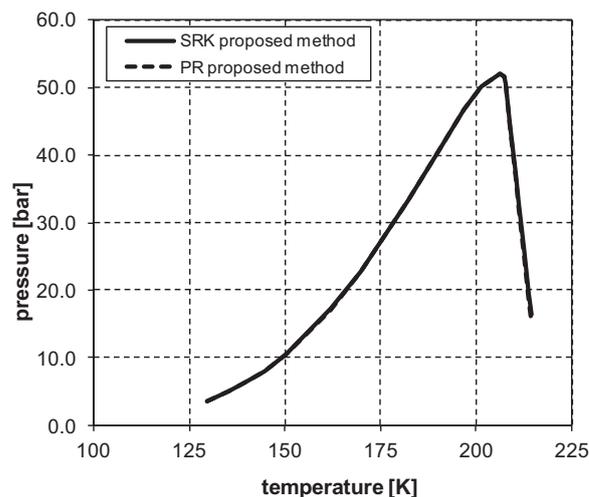


Fig. 3 – Pressure vs. temperature for the solid–liquid–vapor equilibrium of the mixture containing CO₂–methane.

from ASPEN HYSYS® (AspenTech, 2010a) and their values are reported in Table 3.

4. Results and discussion

4.1. Solubility of CO₂ in pure solvents

4.1.1. n-Alkanes

Experimental data of solubility of carbon dioxide in pure n-alkanes containing from one to six carbon atoms (i.e., from methane to n-hexane) are available in the literature (Kurata, 1974) and have been used to compare the obtained results (Fig. 2). The publication by Kurata (1974) reports all available experimental data, also found in other literature sources (Brewer and Kurata, 1958; Davis et al., 1962; Donnelly and Katz, 1954; Eggeman and Chafin, 2003; Jensen and Kurata, 1971).

Experimentally, the solubility of carbon dioxide in the liquid phase increases with temperature, so a higher liquid molar fraction of CO₂ in equilibrium with the solid phase is found. The solubility of carbon dioxide calculated by means of SRK and PR EoSs is in good agreement with experimental data. The Average Absolute Deviations (AAD) calculated according to the following equation:

$$AAD = \frac{\sum_{j=1}^{npt} x_{j,calc} - x_{j,exp}}{npt} \quad (10)$$

are reported in Table 4: they show that the proposed method allows a reliable representation of the thermodynamic equilibrium involving the presence of the solid phase. Moreover, a correct dependence on temperature and component species is obtained, as shown in Fig. 2.

In order to best fit the experimental data, two temperature ranges have been considered for the optimal k_{ij} calculation. In particular, for the system CO₂–methane the temperature range has been divided in correspondence of the inflection point (the temperature value of maximum pressure in the P–T diagram shown in Fig. 3). For the other n-alkanes that do not present an inflection point, the temperature that delimits the considered range is taken at 200 K, i.e., before the solubility curve becomes steep. Results are reported in Fig. 4.

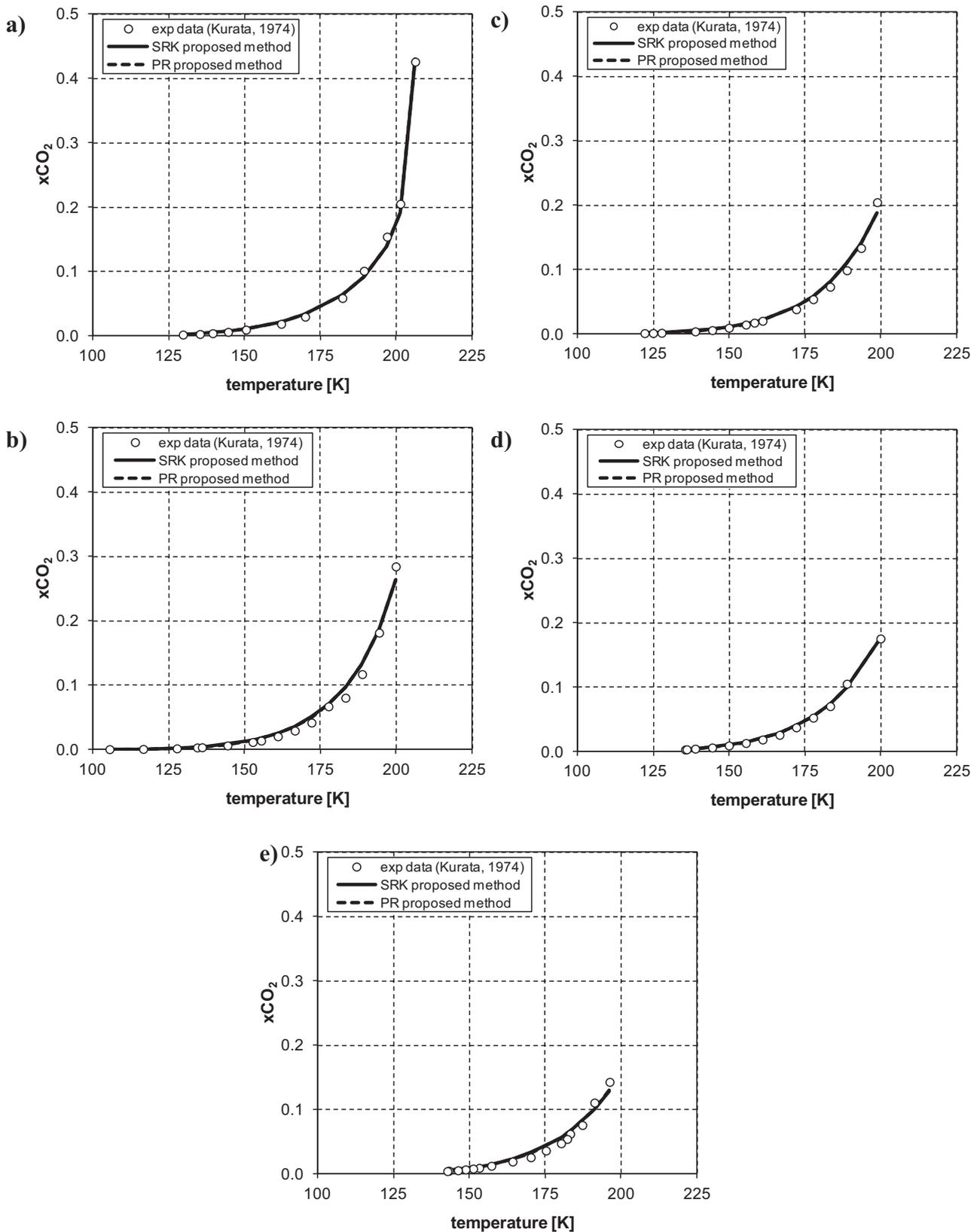


Fig. 4 – Solubility of solid CO₂ in liquid (a) methane, (b) ethane, (c) propane, (d) n-butane, (e) n-pentane, obtained experimentally (Kurata, 1974) and with the proposed method (SRK and PR) considering values of binary interaction parameters regressed in a defined range of temperatures.

4.1.2. Hydrogen sulfide

Solubility data of CO₂ in H₂S have not been found in literature. So proper binary interaction parameters that take into account also the presence of the solid phase cannot be derived. k_{ij} s optimized for vapor-liquid equilibrium have been used but, as

shown in Fig. 5, the results obtained from SRK and PR are quite different. A comparison with the experimental data reported by Sobocinski and Kurata (1959) shows that the predictions obtained when using the SRK equation are more reasonable. However, additional experimental solubility data of CO₂ in H₂S

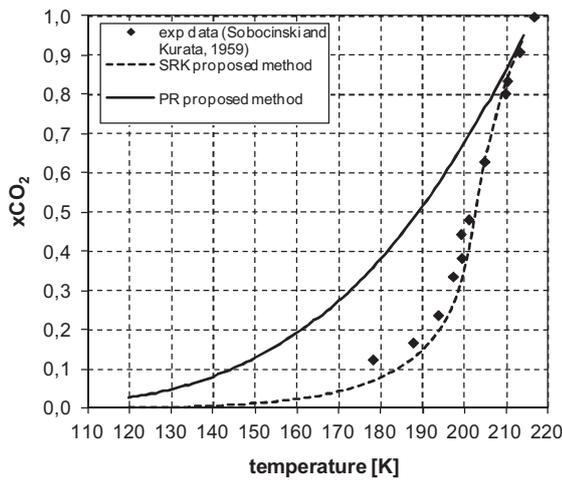


Fig. 5 – Solubility of solid CO₂ in hydrogen sulfide obtained experimentally (Sobocinski and Kurata, 1959) and with the proposed method (SRK and PR).

are needed to better improve the prediction of dry ice formation in systems containing H₂S by the proposed method, since it can represent a safety issue in cryogenic gas purification processes where H₂S is present.

4.2. Solubility of CO₂ in mixtures

4.2.1. Mixtures containing *n*-alkanes

Experimental data of mixtures composed of more than one *n*-alkane and carbon dioxide, as CO₂-CH₄-C₂H₆, CO₂-CH₄-C₃H₈, CO₂-CH₄-C₄H₁₀, CO₂-C₂H₆-C₃H₈ and CO₂-CH₄-C₂H₆-C₃H₈, have been used to validate the proposed method, which is based only on parameters relevant to CO₂ alone (as $\frac{\Delta H_m}{RT_m}$, $\frac{\Delta C_p}{R}$ and T_m) and on the binary interaction parameters k_{ij} s. The obtained AAD and the solubility curve are reported in Table 5 and Figs. 6 and 7, respectively. It can be outsourced that the proposed method allows a reliable representation of the SLV equilibrium: the obtained pairs temperature – x_{CO_2} are in good agreement with experimental data, as shown in Figs. 6 and 7. This is confirmed also by the results reported in Table 5, which shows acceptable values of AAD. The proposed method can easily be extended to mixtures containing a higher number of components. The comparison of multicomponent

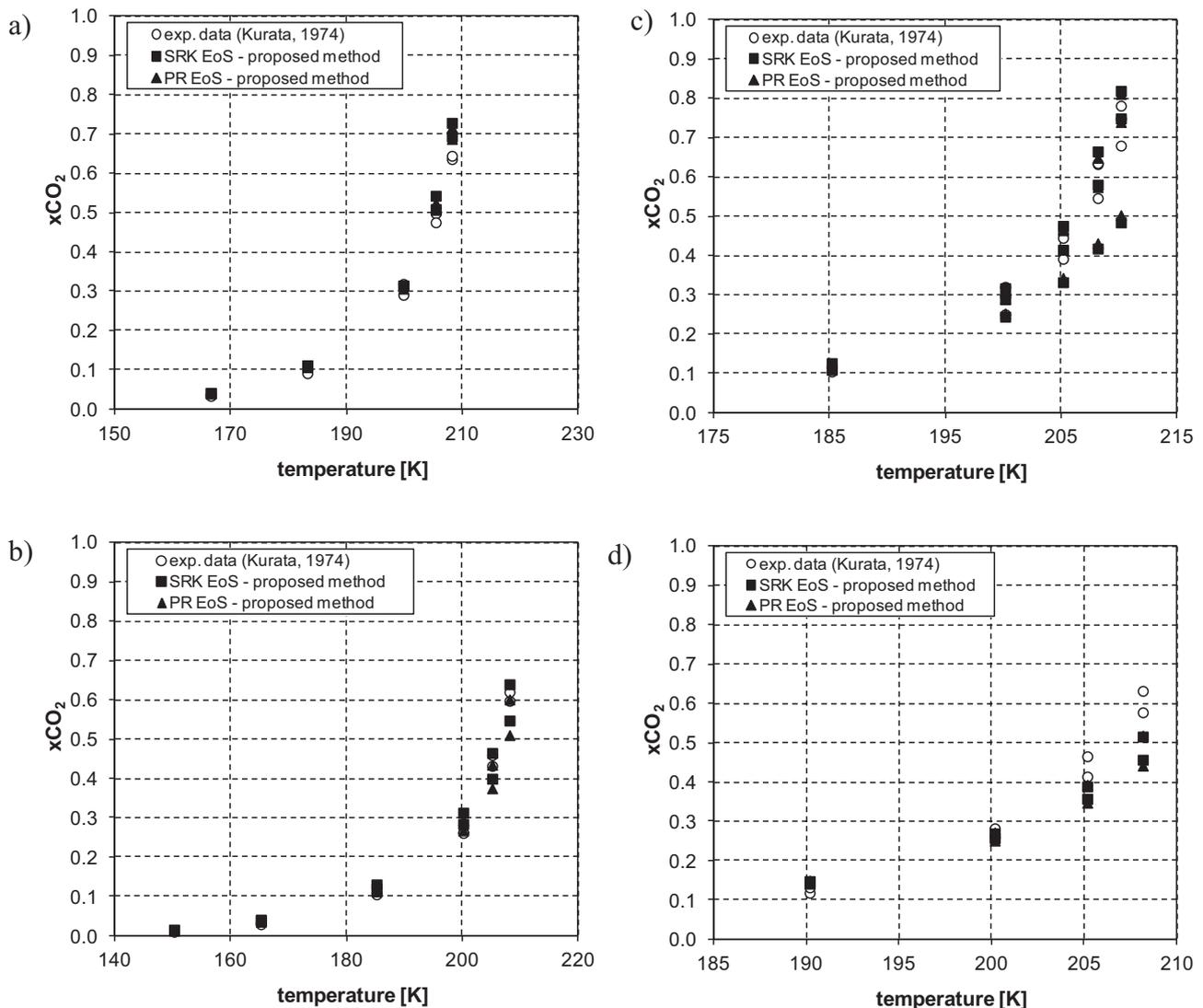


Fig. 6 – Solubility of solid CO₂ in mixture with (a) methane–ethane, (b) methane–propane, (c) methane–*n*-butane, (d) ethane–propane, obtained experimentally (Kurata, 1974) and with the proposed method (SRK and PR).

Table 5 – Average absolute deviations obtained with the proposed method, both with SRK and with PR, for mixtures containing more than one hydrocarbon compound.

Mixture	AAD SRK	AAD PR
CO ₂ -methane-ethane	0.0288	0.0236
CO ₂ -methane-propane	0.0202	0.0217
CO ₂ -methane- <i>n</i> -butane	0.0440	0.0391
CO ₂ -ethane-propane	0.0535	0.0560
CO ₂ -methane-ethane-propane	0.0204	0.0220

experimental data with simulation results has not been extensively performed in literature and this gives, in our opinion, an additional value to the present paper.

4.2.2. Mixtures containing methane and hydrogen sulfide

In this section results of an investigation on carbon dioxide solubility in ternary mixtures containing methane and hydrogen sulfide are discussed with the aim of understanding the effect of the presence of a non-hydrocarbon compound with a higher boiling point than methane, as H₂S is. The analysis has been performed using the proposed method by means of SRK and PR EoSs, by considering mixtures containing a molar fraction of H₂S ranging from 0.05 to 0.35. The effect of hydrogen sulfide is to increase the solubility of carbon dioxide in the liquid phase. Its effect is not linear and it is more evident for concentrations lower than 20% on a molar basis. For H₂S mole fractions greater than 0.2, the solubility of carbon dioxide seems not to be affected anymore by the presence of hydrogen sulfide (Fig. 8).

As in the case of the binary mixture CO₂-H₂S, the more plausible results seem those from SRK, as shown by Fig. 9, which reports solubility data for different H₂S content. The SRK EoS seems to have a better stability whereas the PR EoS gives problems in simulation, pointing out the need of experimental data for this particular system.

4.3. Comparison with other models

For the CO₂-CH₄ binary mixture, the only mixture for which published results have been found in literature, a comparison

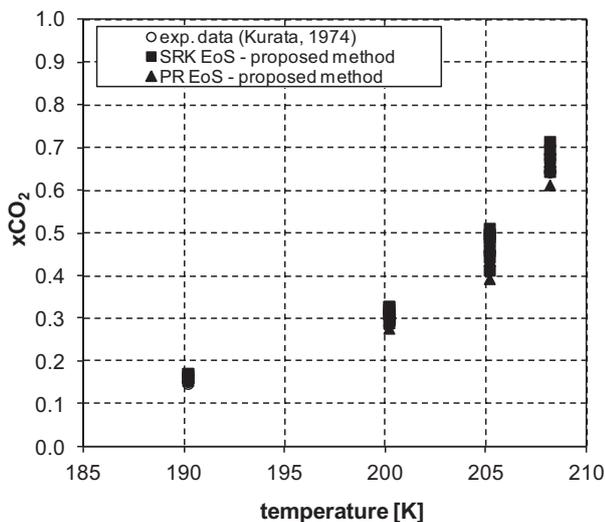


Fig. 7 – Solubility of solid CO₂ in mixture with methane-ethane-propane, obtained experimentally (Kurata, 1974) and with the proposed method (SRK and PR).

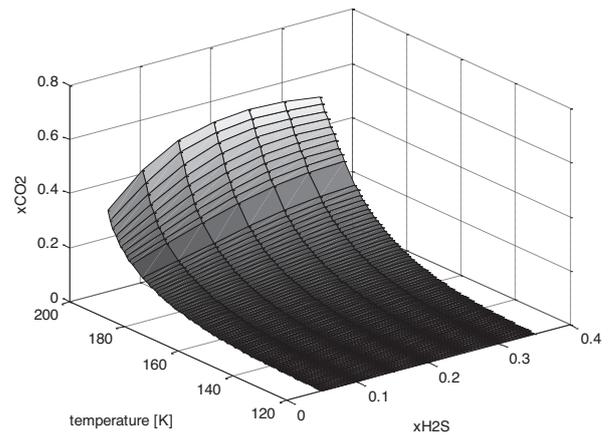


Fig. 8 – Solubility of solid CO₂ in mixture with methane and hydrogen sulfide obtained with SRK EoS in a 3-D plot.

between results obtained with the proposed method, Aspen Plus® PR and SRK EoSs and another model reported in literature (Shen and Lin, 2011) has been reported in Figs. 10 and 11.

Results show that the methodology proposed in this work gives better agreement with experimental data in comparison with the ones obtained with Aspen Plus® and by Shen and

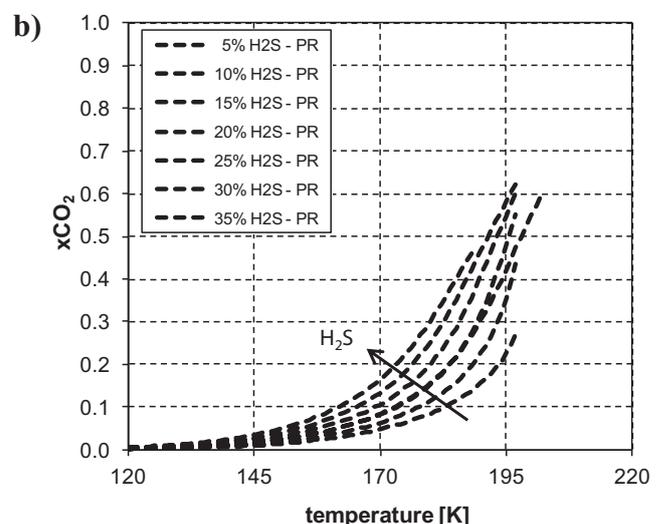
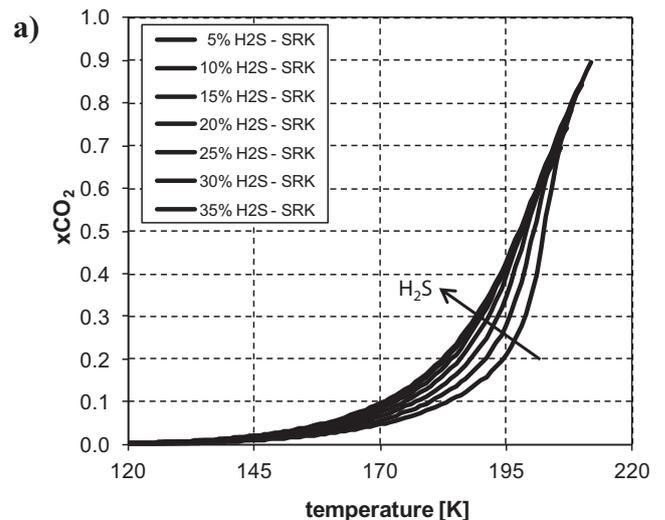


Fig. 9 – Solubility of solid CO₂ in mixture with methane and H₂S, obtained with (a) SRK EoS and (b) PR EoS.

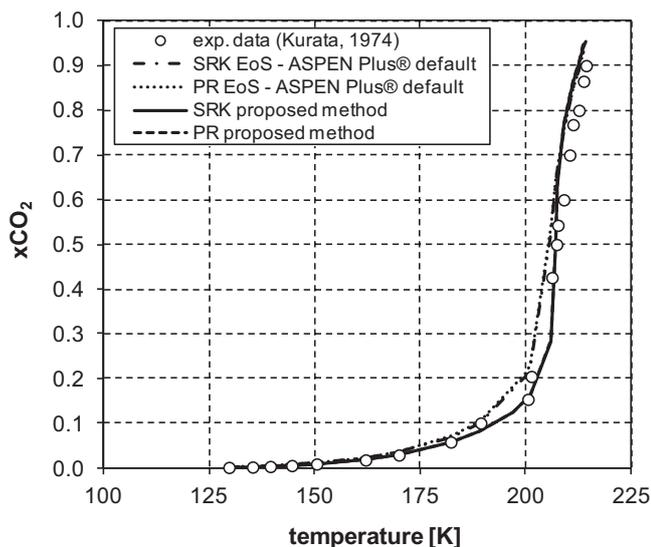


Fig. 10 – Comparison of solubility of solid CO₂ in mixture with methane obtained with the proposed method and with ASPEN Plus® default model.

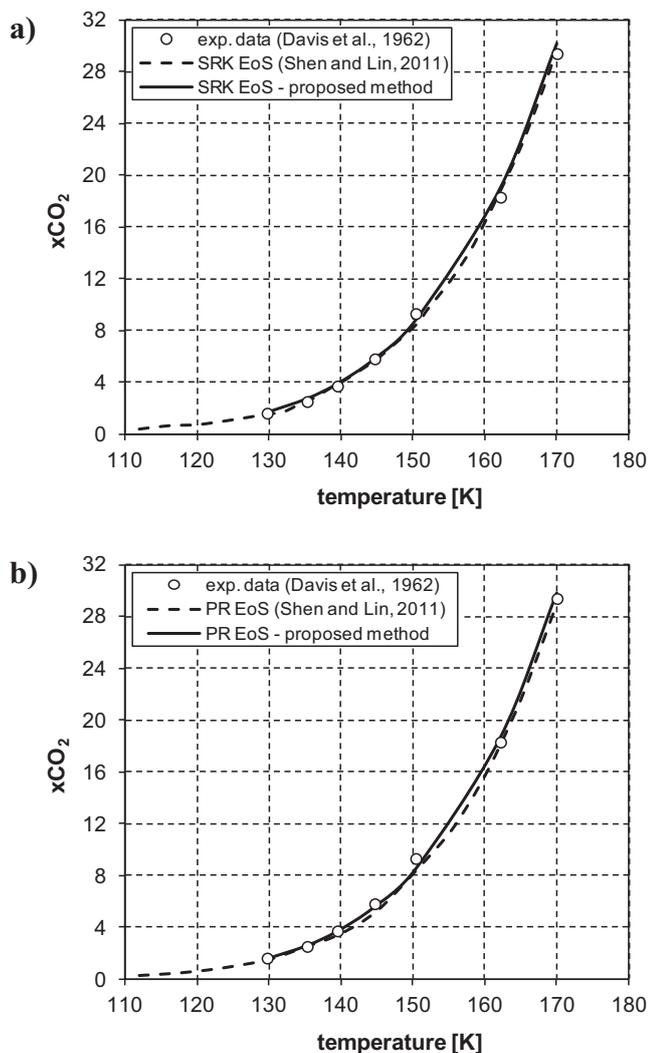


Fig. 11 – Comparison of solubility of solid CO₂ in mixture with methane obtained with the proposed method and with the one by Shen and Lin (2011) for (a) SRK EoS and (b) PR EoS.

Lin (2011), allowing to perform more reliable calculations of carbon dioxide solubility.

5. Conclusions

Carbon dioxide solubility in mixture containing one or more hydrocarbons should be properly predicted, especially when dealing with chemical process design of equipments, where process conditions may lead to the precipitation of a dry ice with consequences on safety.

Cubic Equations of State have been applied to predict solubility of solid CO₂ in systems containing compounds of interest mainly in natural gas purification units. Particular attention has been devoted to obtain an accurate description of the solubility curve for CO₂ binary and multicomponent mixtures, by introducing adaptive parameters.

A regression of experimental data has been performed in order to obtain proper values for SLV equilibrium of single component (CO₂) parameters and of binary interaction parameters, which have been used in the calculations.

The focus of this paper has been a detailed analysis of the method performances when more than two compounds are present in the mixture, since literature does not provide significant modeling results for such cases.

The adopted methodology, then, has been validated by comparison with experimental solubility data of carbon dioxide in liquid mixtures. Section 4 shows the reliability of the obtained results in the representation of the solid–liquid–vapor equilibrium, also for mixtures composed of more than two components.

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