Prediction of carbon dioxide sorption in polymers for capture and storage feasibility analysis

**Abstract**

The carbon dioxide and its capture and storage has found great importance. Polymeric materials have been used for CO2 capture where the solubility of CO2 in polymer is the critical factor that determine the efficiency and performance of selected polymeric materials. For initial assessment and feasibility analysis of considered materials, prior to any experimental measurement, in order to reduce costs, development of a theoretical solubility and sorption model is highly of interest. Thus, here computationally consistent solubility model is developed employing the compressible regular solution theory where inputs parameters include the lattice fluid parameters and Hansen cohesive energy densities that are obtainable using group contribution method of Constantinou and Gani and the group contribution method of van Krevelen respectively. A number of experimental data was collected and used for examination of model accuracy and desirable agreement was found with an *R2* value of 0.9896.

**Keywords**: carbon dioxide; polymer; capture; solubility

# Introduction

Beside its greenhouse gas effect, carbon dioxide (CO2) has a wide potential uses in applications such as enhanced oil recovery (EOR), food and beverage manufacturing, pulp and paper manufacturing, and metal fabrication [[1-3](#_ENREF_1)]. Carbon dioxide capture technologies include absorption with amines, adsorption, membrane gas separation technologies, metal-organic frameworks (MOFs) and etc. [[1](#_ENREF_1),[4](#_ENREF_4)] where solubility of CO2 play a critical role in efficiency and feasibility of technologies, especially in membrane based separations and storage in polymeric materials. Therefore, the determination of solubility of CO2 in polymeric materials is of high importance [[5](#_ENREF_5),[6](#_ENREF_6)]. A substantial number of research works and publications can be found in literature [[7-10](#_ENREF_7)].

In literatures [[5](#_ENREF_5),[7](#_ENREF_7)], the solubility measurements have been done for various polymeric materials and large database of solubility data can be found as in Ref. [[5](#_ENREF_5),[6](#_ENREF_6),[11](#_ENREF_11),[12](#_ENREF_12)]. However, to reduce the cost of experimental measurement and performance evaluation, cost of material preparation and facility maintenance, the development of theoretical models and methods for prediction, prior to any experimental work has found interest in literatures [[7-10](#_ENREF_7),[13](#_ENREF_13)]. Upon establishing such a model, validation of model calculations using any available experimental data is a required need to assess the agreement between model calculated data and those of experimentally measured.

Therefore, here, attempts were made to develop a predictive model employing well-established chemical thermodynamic model of compressible regular solution (CRS) [[14-16](#_ENREF_14)] for local pseudo-equilibrium concentration of penetrant gases within the polymeric material as suitability of CRS theory for polymeric solutions has been demonstrated in literature [[17](#_ENREF_17),[18](#_ENREF_18)]. The details of model development are given in following sections including the data used for model validation. The details of model development and its evaluation are provided in following sections.

# Model development

The amount of penetrant *i* sorped into a polymeric material can be obtained using a local pseudo-thermodynamic equilibrium criterion at the interface of gas bulk stream phase and polymeric material as presented by Eq. 1 [[19](#_ENREF_19),[20](#_ENREF_20),[18](#_ENREF_18)].

|  |  |
| --- | --- |
|  | 1 |

Here,  is the chemical potential of gas component that can be calculated by using thermodynamic theory of compressible regular solution (CRS) model [[15](#_ENREF_15),[14](#_ENREF_14),[16](#_ENREF_16)] and superscripts *m* and *b*, refer to polymeric material and bulk stream respectively.

For the case of single gas sorption, here CO2, the mixture of sorped gas in polymeric material can be considered as a binary mixtures [[17](#_ENREF_17),[21](#_ENREF_21)]. For a binary mixture, the Gibbs free energy model of CRS [[15](#_ENREF_15),[16](#_ENREF_16),[14](#_ENREF_14)] is given by Eq. 2.

|  |  |
| --- | --- |
|  | 2 |

Here, *k* is the Boltzmann constant,  the reduced density of component.  the number of segments in the hard-core volume () of component, the hard-core solubility parameter at 0 K.  is the volume fraction of component. Subscript *i* and *j* refers to gas compound and polymer respectively.

The chemical potential relationship in CRS theory is given by Eq. 3 [[15](#_ENREF_15),[16](#_ENREF_16),[14](#_ENREF_14)].

|  |  |
| --- | --- |
|  | 3 |

In the bulk gas phase, for the calculation of gas chemical potential in bulk phase, as the gas bulk phase is pure (), one might obtain.

|  |  |
| --- | --- |
|  | 4 |

Thus, noting to the equality of chemical potentials in two phases according to Eq. 1, one might obtain Eq. 5.

|  |  |
| --- | --- |
|  | 5 |

Finally, inserting the chemical potential of gas in membrane from Eq. 3 into Eq. 5, carrying out a number of mathematical manipulations, one would obtain Eq. 6.

|  |  |
| --- | --- |
|  | 6 |

Using Mathematica© Software [[22](#_ENREF_22)], the solution to Eq. 6 can be given as in Eq. 7.

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| --- | --- |
|  | 7 |
|  | 8 |
|  | 9 |

Here, is the product log function [[22](#_ENREF_22),[23](#_ENREF_23)], *p* is pressure and noting to expressions in Eq. 8 and Eq. 9 one might write .

the Taylor series expansion of product log function, , can be used to simplify Eq. 7 using Mathematica© Software [[22](#_ENREF_22)].

|  |  |
| --- | --- |
|  | 10 |

Therefore, Eq. 7 reads Eq. 14.

|  |  |
| --- | --- |
|  | 11 |
|  | 12 |
|  | 13 |
|  | 14 |

The volume fraction, then can be converted to the solubility coefficient noting that = andwhere *p* is the pressure.

# Method of calculations

The , hard-core solubility parameter, can be calculated using the Hoftyzer and van Krevelen group contribution method [[24](#_ENREF_24)]. The reduced density, then can be calculated as and the hard-core solubility parameter can be calculated as [[18](#_ENREF_18)]. The superscript and subscript *0* indicates the reference temperature of 298 K [[18](#_ENREF_18)]. The quantity  can be calculated using where  is the molecular weight of component (for polymer, the repeating unit) [[18](#_ENREF_18)]. The  is the lattice-fluid (LF) scaling constant of Sanchez and Lacombe Equations of State (SL EOS) [[25](#_ENREF_25)] and can be calculated using the group contribution method of Constantinou and Gani [[26](#_ENREF_26)] modified by Boudouris et al. [[27](#_ENREF_27)].

The recued density can be obtained from the modified version of SL EOS [[27](#_ENREF_27)] presented by Eq. 15. By an initial guess of, Eq. 15 can be solved numerically using an iterative root seeking method for any temperature and pressure condition of interest.

|  |  |
| --- | --- |
|  | 15 |

Here,,  are reduced pressure, temperature, density of lattice-fluid (LF) given by Eq. 16 [[27](#_ENREF_27)].

|  |  |
| --- | --- |
|  | 16 |

Here, ,  and  are characteristic pressure, temperature and density developed by Boudouris et al. [[27](#_ENREF_27)] for SL EOS.

A detailed step-by-step application of developed method follows.

1. Select the penetrant gas of interest (CO2 here) and the polymeric material considered,
2. Determine the chemical structure of penetrant gas and polymer repeating unit selected in # ‎1,
3. Calculate lattice fluid parameters using group contribution method of Constantinou and Gani [[28](#_ENREF_28)] utilizing the chemical structure of # ‎2,
4. Calculate solubility parameters at reference temperature (298 K) using van Krevelen group contribution method [[29](#_ENREF_29)] utilizing the chemical structure of # ‎2,
5. Calculate reduced hard core densities of penetrant gas and polymer by inserting lattice fluid parameters of # ‎3 in the SL-EOS [[25](#_ENREF_25),[30](#_ENREF_30)] and solving it using an iterative root seeking method,
6. Calculate solubility parameters at operating temperatures using data of # ‎5,
7. Calculate as ,
8. Calculate the penetrant content () within the membrane at the condition of interface of gas bulk stream phase and polymeric material by inserting data of #‎3-‎7 in Eqs. 8-9 and pressure at the interface in Eq. 14,
9. Convert calculated concentrations from # ‎8 to the solubility coefficient as = where  and *p* is the pressure,

# Collected data and model validation

For model validation, the solubility data were collected from Ref. [[7](#_ENREF_7)]. The required lattice fluid parameters for model calculations are listed in **Table 1** and **Table 2** respectively for CO2 and considered polymers.

**Table 1.** Lattice fluid parameters and required data of carbon dioxide [[7](#_ENREF_7),[31](#_ENREF_31)]

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Compound** | **/ K** | **/ MPa** | **/ g/cm3** | **/ MPa0.5** | **/ cm3/mol** |
| CO2 | 300 | 630 | 1.515 | 25.84 | 110.8 |

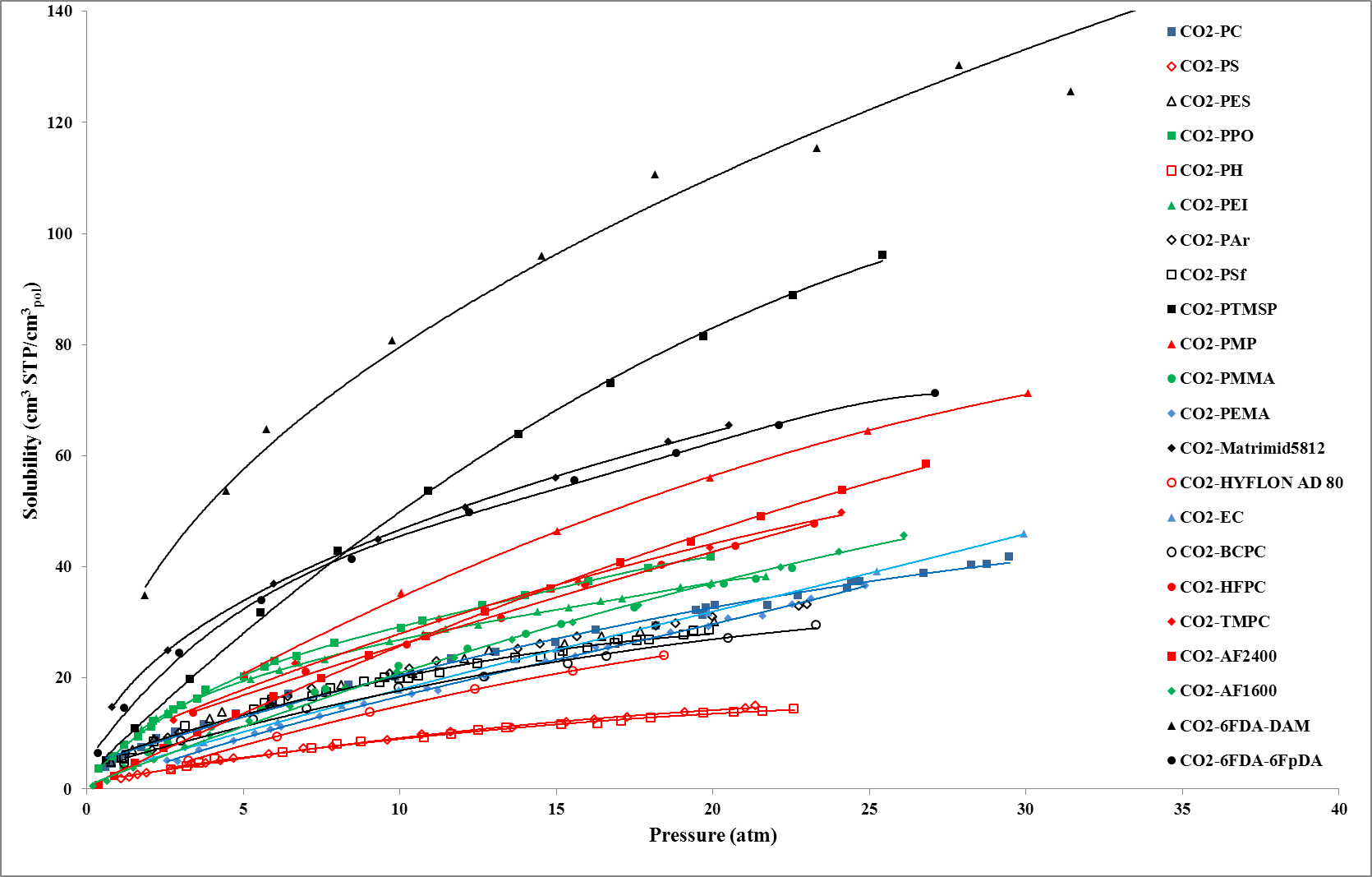
**Table 2.** Lattice fluid parameters of considered polymers [[7](#_ENREF_7),[17](#_ENREF_17)]

|  |  |  |  |
| --- | --- | --- | --- |
| **Compound** | **/ K** | **/ MPa** | **/ g/cm3** |
| AF1600 | 610 | 245 | 2.085 |
| AF2400 | 624 | 250 | 2.13 |
| HYFLON AD80 | 550 | 180 | 2.15 |
| 6FDA-DAM | 765 | 480 | 1.66 |
| 6FDA-6FpDA | 785 | 720 | 1.683 |
| Ethyl cellulose (EC) | 620 | 515 | 1.231 |
| Matrimid | 880 | 450 | 1.350 |
| Polycarbonate (PC) | 755 | 534 | 1.275 |
| Polysulfone (PSf) | 830 | 600 | 1.31 |
| Polymethylmethacrylate (PEMA) | 602 | 507 | 1.221 |
| Polymethylmethacrylate (PMMA) | 695 | 560 | 1.27 |
| Poly1-trimethylsilyl-1-propyne (PTMSP) | 416 | 405 | 1.25 |
| Poly4-methyl-2-pentyne (PMP) | 550 | 360 | 1.04 |
| Polyetherimide (PEI) | 615 | 690 | 1.245 |
| Polyarilate (PAr) | 855 | 640 | 1.457 |
| Polyhydroxyether (PH) | 760 | 576 | 1.31 |
| Polyethersullfone (PES) | 739 | 479 | 1.177 |
| Polyphenyleneoxide (PPO) | 750 | 360 | 1.099 |
| Polystyrene (PS) | 820 | 610 | 1.384 |
| Bisphenolchloral polycarbonate (BCPC) | 700 | 670 | 1.52 |
| Tetramethylpolycarbonate (TMPC) | 730 | 480 | 1.191 |
| Hexafluoropolycarbonate (HFPC) | 716 | 446 | 1.618 |
| ***AF2400***: 65 mol% 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole and 35 mol% tetrafluoroethylene (random copolymer); ***AF1600***: 87 mol% 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole and 13 mol% tetrafluoroethylene (random copolymer); ***6FDA-6FpDA***: 2,2-bis(3,4-carboxyphenyl) hexafluoropropane dianhydride, 4, 4-Hexafluoro diamine polyimide; ***6FDA-DAM***: 2,2-bis(3,4-carboxyphenyl) hexafluoropropane dianhydride, diaminomesitylene polyimide; ***HYFLON AD80***: 85 mol% 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole and 15 mol% perfluorodioxole (random copolymer) | | | |

# Results and discussion

For each considered polymer, the solubility calculations were performed and results are shown in **Fig.1** demonstrating the suitability of developed method for calculation of solubility coefficients. The model inputs are the lattice fluid parameters of gas and the polymer which are available in literature [[17](#_ENREF_17)] or can be simply calculated using group contribution methods [[27](#_ENREF_27)]. The Hansen solubility parameters are already complied by Hansen in Ref. [[31](#_ENREF_31)] for a large database of polymers and even can be simply calculated using group contribution methods [[29](#_ENREF_29)]. Therefore, model implementation for any system of interest is simple and readily accessible without the need of adjustable parameters or the availability of experimental data. Having the chemical structure of gas (here CO2) and repeating unit of polymeric material, the developed method can be simply used following the illustrated procedure.

The developed model used the compressible regular solution (CRS) chemical theory which has found various applications where the polymeric solutions have been under study and showed great reliability and accuracy in description of polymeric solution phase behavior [[17](#_ENREF_17),[18](#_ENREF_18)]. Based on the model calculation results shown in **Fig.1**, the application of model is feasible and with desirable accuracy, therefore it can be used for estimation of solubility data and prior assessment of various polymers that are candidate for CO2 capture applications.



**Fig.1**. Solubility of CO2 in various polymers: bullets show experimental data and solid lines show the model prediction

To evaluate the agreement between the experimental and calculated data, four statistical parameters including sum of squares due to error of the fit (SSE), square of the correlation (R2), adjusted R-square (R2-adj) and standard error of the regression (RMSE) were implemented [[13](#_ENREF_13)] as summarized in Table 3.

Table 3. Statistical parameters [[13](#_ENREF_13)]

|  |  |
| --- | --- |
| **Parameter** | **Equation** |
| sum of squares due to error of the fit |  |
| square of the correlation |  |
| adjusted R-square |  |
| standard error of the regression |  |
| ***Note*:** *n* is number of data and *m* is number of coefficient in the models (*m*=0). | |

The statistical parameters values are summarized in Table 4.

Table 4. Statistical parameters

|  |  |
| --- | --- |
| **Parameter** | **Value** |
| SSE | 0.1763 |
| R-sq. | 0.9896 |
| adjusted R-sq. | 0.9896 |
| RMSE | 0.1952 |

# Conclusion

For prior assessment of suitability of polymeric materials for CO2 capture applications, a reliable predictive and easy-to-use solubility model was developed employing the compressible regular solution (CRS) chemical theory and examined for a number of polymeric materials. The model uses lattice fluid parameters and Hansen cohesive energy densities of CO2 and polymeric materials. For a number of collected systems, the applicability and predictive capability of model was examined and desirable agreement was found. Therefore, the model can be used for assessment of any selected polymer to evaluate its potential for CO2 capture application.

# List of notations

|  |  |  |
| --- | --- | --- |
|  |  | Gibbs free energy |
|  |  | Boltzmann constant |
|  |  | the molecular weight of components |
|  |  | Product of number of hard cores in molar volume of each core |
|  |  | Pressure |
|  |  | reduced pressure (hard-core pressure) |
|  |  | the universal gas constant |
|  |  | Temperature |
|  |  | reduced temperature (hard-core temperature) |
|  |  | density |
|  |  | reduced density (hard-core density) |
|  |  | Scaled density the modified Sanchez-Lacombe Lattice Fluid model (SL-LF) in Boudouris et al. |
|  |  | Solubility parameter |
|  |  | solubility parameter in 298 K |
|  |  | Chemical potential |
|  |  | Difference in property |

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