Evaluation of CO₂ and CH₄ Solubilities in PVDF by Molecular Simulation: a Comparison of Various Methods

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Résumé — Évaluation par simulation moléculaire des solubilités de CO₂ et CH₄ dans le PVDF : comparaison de diverses méthodes — Cet article présente une comparaison des techniques de simulation moléculaire permettant d'évaluer les solubilités de CO₂, CH₄ et leurs mélanges, à diverses températures et pressions, dans un polymère semi-cristallin fluoré, le fluorure de polyvinylidène (PVDF). Nous avons utilisé des outils de simulation commerciaux fournis par la société Accelrys Inc. Nous avons toutefois dû développer des protocoles de simulation spécifiques afin d'obtenir des résultats fiables. Ces résultats sont en bon accord avec l'expérience. Enfin, nous discutons la nature des interactions qui déterminent la solubilisation de CO₂ et CH₄ dans le PVDF, phénomène important à prendre en compte pour la conception de lignes flexibles composites destinées au transport de fluides de production pétroliers et gaziers en conditions extrêmes.

Abstract — Evaluation of CO₂ and CH₄ Solubilities in PVDF by Molecular Simulation: A Comparison of Various Methods — Molecular simulation techniques were compared to evaluate the solubilities of CO₂ and CH₄ and mixtures in polyvinylidene fluoride (PVDF), a fluorinated semicrystalline polymer, in various T and P conditions. We have used commercial tools available from Accelrys Inc. However, it was necessary to develop a specific simulation protocol in order to get reliable results. These results compare well with experiments. We discuss finally the nature of interactions which determine the solubilization of CO₂ and CH₄ in PVDF, an important issue for the design of armoured flexible pipelines dedicated to oil and gas production fluids in extreme conditions.
1 OBJECTIVES AND SCOPE OF WORK

The objectives of our work were two fold:

1. to investigate the interactions between solubilized gases and the polymer matrix;
2. to assess the ability of molecular simulation techniques to generate solubility data for gas-polymer systems without experimental input.

In molecular simulations, the interactions are determined by the choice of an empirical force field. A “force field” means the approximate representation of the potential energy of an ensemble of atoms considered as a function of the spatial coordinates of all atoms. A given force field is characterized by its functional form, and the associated numerical parameters. As the simplest example, one can figure out the harmonic oscillator model as a force field describing an isolated diatomic. In that case, the functional form is quadratic in deviation from equilibrium distance, and the parameters are the force constant, the equilibrium distance, and the mass of atoms. State of the art force fields, such as CVFF (Consistent Valence Force Field), UFF (Universal Force Field), PCFF (Polymer Consistent Force Field) and COMPASS (Condensed Phase Optimized Molecular Potential for Atomic Simulation Studies), developed and distributed by Accelrys [1], or Dreiding, MM3, which are freely available, include many terms to represent the intramolecular contributions to potential energy (bond stretchings, bond bendings, torsions around one bond, cross terms) and the intermolecular contributions (attractive dispersion forces, short range repulsive forces, coulombic interactions, hydrogen bonds optionally). The chemical diversity is accounted for by differentiating atom types according to their bonding environment: for instance, usually 3 types will be distinguished for carbon in hydrocarbons according to the hybridization state (sp3, sp2, sp), but more types will be necessary to account for C in –C = O, –COOH or –C–OH groups. Therefore, a forcefield of general purpose for organic chemistry will necessitate a very sizeable set of parameters to be determined. These parameters are based both on experimental data (structural and spectroscopic for example), and on high quality ab initio calculations. The parameters of a force field must be transferable, that is to say one should be able to predict accurately the geometric and vibrational properties of any molecule outside of the “training set” (set of molecules involved in the fitting procedure).

The best way to assess the quality of a force field for a given molecular system is to use simulations to generate synthetic experimental data, that is quantities measurable on the real system. Therefore, in the present project, it appeared soon that steps 1 and 2 should be reversed, so that the comparison of simulated with experimental solubility data having allowed the selection of the best suited force field, confidence might be placed in the latter to obtain insight on the nature of the local interactions between gases and the polymer matrix.

In a first part of the study, we have concentrated on the definition of a protocol to build representative atomistic models of amorphous PVDF, and to select both the best force field and the best methodology in order to evaluate solubilities of pure CO2 and CH4. This choice was based on the generally admitted assumption that the solubility of a gas in the crystalline fraction of a semicrystalline solid polymer is negligible. Hence, upon comparing simulated and experimental data, the latter have to be divided by the experimentally determined volume fraction of amorphous phase.

After a protocol was identified which gave a reasonable match between simulated and experimental solubilities, we started a preliminary study of the solubilities for binary gas mixtures.

Finally, we were able to identify and rank the various components of the solute-matrix interactions for these systems, as represented by the force field producing the best predictions of solubilities.

2 METHODS

2.1 Hardware and Software

All calculations were performed on an Octane Silicon Graphics workstation fitted with a R10000 RISC microprocessor and 128 MB main memory.

The software modules were furnished by Accelrys Inc. [1], as a benefit of IFP’s membership in the consortium “Polymer 2000”. We made use of the two UNIX graphical interfaces “Cerius2” and “InsightII”. PVDF amorphous cells were built with the modules “polymerizer” and “amorphous cell”. Polymerizer enables to build a chain of given characteristics (degree of polymerization, tacticity, etc.) with a “repeat-unit” (monomer) as a starting point. Amorphous cell implements a Monte-Carlo chain growth procedure to pack a chain into a cell of preset volume (thus specifying a density) and to which periodic boundary conditions are applied. The resulting model has to be brought closer to thermodynamic equilibrium through molecular dynamics (MD) runs which were performed thanks to the “Discover 3” module. The WIMC (widom insertion Monte-Carlo) and TST (Gusev and Suter transition state theory) methods were accessible within the “Gsnnet” and “Gsdff” modules. The GCMC method was implemented in the “sorption module”.

Typically, systems including 1000 to 5000 atoms were tractable routinely. Calculations were very intensive, with durations of the order of 48-72 h for the most demanding (MD equilibrations and GCMC (grand canonical Monte-Carlo method)) being more the rule than the exception.

2.2 Force fields

We have essentially compared the two force fields PCFF and COMPASS specially developed by Accelrys within the
“Polymer Consortium” to represent interactions in polymeric systems. The full energy expression in PCFF is given by Equation (1):

\[
E_{\text{Total}} = \sum_{j} \left[ K_2 (b-b_0)^2 + K_3 (b-b_0)^3 + K_4 (b-b_0)^4 \right] \\
+ \sum_{\varnothing} [H_2 (\Theta - \Theta_0)^2 + H_3 (\Theta - \Theta_0)^3 + H_4 (\Theta - \Theta_0)^4] \\
+ \sum_{\varnothing} [V_1 (1 - \cos \Phi) + V_2 (1 - 2 \cos \Phi) + V_3 (1 - 3 \cos \Phi)] \\
+ \sum_{\varnothing} K(\chi - \chi_0)^2 + \sum_{b} \sum_{b'} F_{b b'} (b-b_0)(b'-b_0') \\
+ \sum_{\varnothing \varnothing} F_{\Theta \Theta} (\Theta - \Theta_0)(\Theta' - \Theta'_0) + \sum_{\varnothing} F_{\Phi \Phi} (b-b_0)(\Theta - \Theta_0) \\
+ \sum_{\varnothing} \sum_{\varnothing} F_{b b'} (b-b_0) (1 - \cos \Phi) + F_{b b'}^2 (1 - 2 \cos \Phi) \\
+ \sum_{\varnothing \varnothing} \sum_{\varnothing \varnothing} K_{b b'} (\cos \Phi - \Theta_0)(\Theta' - \Theta'_0) \\
+ \sum_{i \neq j} \frac{q_i q_j}{e_{ij} r_{ij}} + \sum_{i \neq j} \frac{e_{ij}}{2} \left( \frac{r_{ij}^*}{r_{ij}} \right)^9 - 3 \left( \frac{r_{ij}^*}{r_{ij}} \right)^6 
\]

In this expression, the last two terms account for intermolecular interactions, i.e. coulombic and van der Waals, while the other terms represent intramolecular components of the potential energy. The functional form for COMPASS is the same, but parameters differ somewhat, and particularly the sets of intermolecular parameters \( q_i \) (partial atomic charges assigned to individual atoms) \( e_i \) (depth of the van der Waals self-interaction potential well for atom \( i \)) and \( r_{ij}^* \) (distance of maximum attraction between two atoms of type \( i \)).

### 2.3 Building PVDF Model Amorphous Cells

We have built the repeat-unit \( -\text{CH}_2-\text{CF}_2-\text{t} \) as the building block of our model PVDF. The letters \( h \) and \( t \) label the head and tail sides of this repeat-unit respectively. Using the Polymerizer module of InsightII we have built linear isotactic chains in the \( h-t-h-t \) ... sequence, neglecting the sequencing defects which are estimated to occur with a probability below 0.05 in the real polymer.

As \( M_w \) of PVDF is usually in the range 150 000-500 000 g·mol\(^{-1}\) the degree of polymerization DP is in the range 2300-7800, and a chain comprises 14 000 to 47 000 atoms. In order to minimize computer time, we have looked for the minimum DP yielding an acceptable density \( d \) for the packed amorphous cell. We make use here of the results of Rigby et al. [2] for PEO and COMPASS showing that \( d \) is increasing with DP of the model polymer, but reaches a plateau.

The polydispersity index (IP) of real PVDF may vary in the range 1-20. Neglecting that characteristic for a start we have built amorphous cells by specifying the chain DP, the number of chains per cell, and a initial density \( d_i \) at target temperature \( T \) and pressure \( P \). The cell initial volume is therefore fixed, and the filling procedure can be initiated in the Amorphous Cell module: this procedure involves a step by step growth of chains. Overlaps and configurations too high in energy are eliminated thanks to a Monte-Carlo sampling procedure. A “look-ahead” option according to Theodorou and Suter [3] improves the efficiency of the process.

This initial amorphous cell has to be further equilibrated, or “refined” to provide more realistic configurations. The initial density is always set to a lower value than the target experimental density \( d_r \) at \( T \) and \( P \) in order to allow the model system to reach equilibrium through contraction instead of expansion. Reaching a realistic \( d_r \) is critical for solubility evaluations as it will determine the free volume of the model amorphous polymer, which in turn determines the space available for host molecules: there is an intimate link between solubility and free volume in an amorphous polymer, and not only free volume, but its spatial distribution. The latter should be accurately reproduced in principle in order to provide a satisfying model as regards solubility and diffusivity evaluations, and thus the ultimate quantity to be predicted: permeability.

After a number of trials and error, and thanks to experience shared within the “Accelrys Polymer 2000 Consortium”, we have finally frozen the following refining procedure, which yielded the best results for PVDF:

1. energy minimization (~1000 steps);
2. molecular dynamics in the \( NVT \) ensemble (\( T \) target temperature, \( V \) initial) 8000 steps;

![Figure 1](image-url) Front view of an equilibrated model PDVF amorphous cell.
3 molecular dynamics (MD) in the NPT ensemble (T target
temperature, P target pressure) 8000 steps;
4 final molecular dynamics run in the NPT ensemble,
80 000 steps.

A MD step is a timestep of 1 femtosecond (10-15 s). T is
temperature, P is controlled thanks to the Andersen method, and P is controlled
the Berendsen method. The latter restricts the cell unit-vectors to be orthonormal.

A front view of an equilibrated PVDF amorphous cell is
defined in Equation (2). Notice

\[ N \Delta H = - \sum_{i}^{N} \Delta U / kT \]  

(2)

The difficulty here is to ensure a correct sampling, and
usually convergence is poor even a very large number N
of trial insertions.

\[ P_{\text{add}} = \min \left( \frac{PV}{(N + 1)kT} \exp(-\Delta U / kT); 1 \right) \]  

(3)

\[ P_{\text{delete}} = \min \left( \frac{NkT}{PV} \exp(-\Delta U / kT); 1 \right) \]  

(4)

The average number \( \langle N \rangle \) of molecules inserted per
unit-cell is a direct estimate of the solubility S through:

\[ S = \frac{\langle N \rangle}{P} \]  

(5)

And the Henry constant can be derived from:

\[ H = \lim_{P \to 0} \frac{\langle N \rangle}{P} \]  

(6)

According to the GCMC method, it is possible to reconst-
struct the full solubility isotherm, by varying the host fugacity step by step, at the expense of a sizeable amount of compu-
ting resource. For comparison with experimental data obtained
for high total or partial pressures of host molecules, care
should be taken to relate properly the measured pressure to
the fugacity. To that end we have used the Peng-Robinson
equation [6]. In order to get reasonably converged averages,
of the order of 5.10^6 to 10^7 Monte-Carlo moves are neces-
sary. This implies that the GCMC method is by far the most
compute intensive.

3 RESULTS

3.1 PVDF Amorphous Cells: Reproducibility and
Representativity

According to tables [7] and estimates given by the Synthia
method [8], the density of amorphous PVDF at 298 K is
equal to 1.6 g·cm^{-3}. Using the procedure described above in
Section 2.3, and varying DP, we have not found a very clear
tendency for density to increase with DP. If we consider
however that the model with the highest DP is the most
representative, we can compare results obtained with DP = 100 at 298 K and under a fugacity of 5 bar for the two force fields. COMPASS (in the version used for these calculations) gave \( d = 1.4 \text{ g cm}^{-3} \) and PCFF was consistently better with \( d = 1.61 \text{ g cm}^{-3} \). Improvements were obtained with COMPASS when a further version was released, which included refined parameters for fluorine. In what follows, we discuss results obtained with the PCFF force field.

### 3.2 Results at \( f = 5 \text{ bar} \) and \( T = 298 \text{ K} \), Pure Gases

The results obtained with the different methods are compared in Table 1. Obviously the Monte-Carlo methods are rather consistent, while the TST method yields results higher by an order of magnitude.

**Table 1**

<table>
<thead>
<tr>
<th></th>
<th>( S \text{CH}_4 )</th>
<th>( S \text{CO}_2 )</th>
<th>( S \text{CO}_2 / S \text{CH}_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TST</td>
<td>1.46</td>
<td>6.7</td>
<td>4.6</td>
</tr>
<tr>
<td>WIMC</td>
<td>0.2</td>
<td>0.91</td>
<td>4.48</td>
</tr>
<tr>
<td>CGMC</td>
<td>0.22</td>
<td>0.88</td>
<td>3.89</td>
</tr>
</tbody>
</table>

### 3.3 Results at \( f = 40 \text{ bar} \) and \( T = 408 \text{ K} \), Pure Gases

The results obtained in those conditions are compared in Table 2.

**Table 2**

<table>
<thead>
<tr>
<th></th>
<th>( S \text{CH}_4 )</th>
<th>( S \text{CO}_2 )</th>
<th>( S \text{CO}_2 / S \text{CH}_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TST</td>
<td>0.29</td>
<td>0.77</td>
<td>2.63</td>
</tr>
<tr>
<td>WIMC</td>
<td>0.07</td>
<td>0.11</td>
<td>1.6</td>
</tr>
<tr>
<td>CGMC</td>
<td>0.07</td>
<td>0.08</td>
<td>1.28</td>
</tr>
</tbody>
</table>

The same remarks as in Section 3.2 apply. We notice an influence of \( T \) and \( P \) conditions not only on the solubilities, but also on the predicted selectivity.

### 3.4 Results at \( f = 40 \text{ bar} \) and \( T = 293 \text{ K} \), Mixture 50% \( \text{CO}_2 + 50% \text{CH}_4 \)

A distinctive capability of the GCMC method is that it allows to study sorption equilibria for mixtures: it suffices to insert and delete the molecules present in the mixture with the appropriate frequencies. The simulation accounts properly for guest-guest interactions inside the host as a function of loading. Once again however, the partial fugacities and not the partial pressures set the relevant chemical potentials. We performed only GCMC simulations in order to explore the composite isotherm. The results are shown in Table 3.

**Table 3**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>408</th>
<th>298</th>
<th>293**</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S \text{CO}_2 ) (expt. A)</td>
<td>0.57</td>
<td>1.7</td>
<td>n.d.</td>
</tr>
<tr>
<td>( S \text{CH}_4 ) (expt. A)</td>
<td>0.1</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>( S \text{CO}_2 / S \text{CH}_4 ) (expt. A)</td>
<td>6.0</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>( S \text{CH}_4 ) (expt. B)</td>
<td>(-0^*)</td>
<td>(-0^*)</td>
<td>n.d.</td>
</tr>
<tr>
<td>( S \text{CO}_2 ) (expt. B)</td>
<td>0.085*</td>
<td>0.613*</td>
<td>0.86*</td>
</tr>
<tr>
<td>( S \text{CO}_2 ) (GCMC)</td>
<td>0.088</td>
<td>0.88</td>
<td>0.82</td>
</tr>
<tr>
<td>( S \text{CH}_4 ) (GCMC)</td>
<td>0.07</td>
<td>0.22</td>
<td>0.06</td>
</tr>
<tr>
<td>( S \text{CO}_2 / S \text{CH}_4 ) (GCMC)</td>
<td>1.0</td>
<td>4.0</td>
<td>15.0</td>
</tr>
</tbody>
</table>

* Corrected for an Arrhenian temperature dependence, and for the experimental crystallinity of 39.8%.
** Mixtures \( \text{CO}_2 + \text{CH}_4 \). The most significant results are highlighted. “n.d.”: not determined.

### 4 COMPARISON WITH EXPERIMENTS AND DISCUSSION

A collaboration developed between IFP and the University of Thessaloniki provided a unique opportunity to compare the prediction of molecular simulations with direct experimental measurements of solubilities by the gravimetric method (quartz crystal microbalance apparatus) in comparable conditions [10]. Otherwise, indirect measurements were available from desorption experiments: the solubility is related in that case to the flux desorbed from the polymer sample in the linear regime occurring in the limit of long time. It is thus model dependent.

The experimental data were available from IFP databases [9] or taken from ref [10]. In order to exploit the latter, we determined first the Henry constants by linear regression of the isotherm as a function of pressure. We estimated further the temperature dependence of Henry constants with an Arrhenius law. Experimental solubilities given in g per 100 g of polymer were converted into cm\(^3\) (STP)·cm\(^{-3}\) taking a density of 1.6 g·cm\(^{-3}\) for the amorphous polymer and the measured crystallinity of 39.8% vol. on samples as exposed. We assume in all cases that the gases are insoluble in the crystalline phase.
The comparison is presented in Table 3. In that table we retained only the simulation results obtained according to the GCMC method. The solubility of CH₄ was found below detection limit with the gravimetric method, therefore no figure is provided.

In Table 3, the most significant results have been highlighted, namely the solubility figures for CO₂ at 298 and 408 K obtained from the direct experiment and predicted by GCMC simulation. The correspondence is surprisingly good, in view of the accumulated sources of possible errors. In the present state of our practice, an estimate of solubility by GCMC is reproducible with a standard deviation over mean ratio of about 30%. Therefore, confidence should be given mostly to the order of magnitude predicted, when one considers only an isolated simulation. In the present case however, the figures given are averages over N repeated simulations, which reduces the uncertainty by a factor N⁻¹/₂.

By contrast with direct experiment, GCMC does predict a non zero solubility of CH₄ in PVDF, in agreement with the desorption indirect method. Kinetic limitations may have prevented the gravimetric experiments to reach true equilibrium, or a problem of sensitivity might have arisen. This point should deserve further verification.

In the case of experiments and simulations involving mixtures we also get a satisfying agreement, with the caveat that the real situation only an isolated simulation. In the present case however, the figures given are averages over N repeated simulations, which reduces the uncertainty by a factor N⁻¹/₂.

It is now possible to discuss the origin of the different behaviors of CO₂ and CH₄ with respect to PVDF in terms of molecular interactions: because the GCMC is not a model dependent method excepted for the force field used, and considering the good predictive capability of PCFF, one can conclude that the latter provides realistic and accurate representations of intermolecular interactions.

The symmetric matrices presented in Tables 4 and 5 summarize these interactions in terms of the parameters of all pairwise atomistic interactions in the system. The functional form for nonbonded interactions in PCFF is given by the last two terms of Equation (1):

\[
E_{\text{intermolecular}} = \sum_{i>j} q_i q_j \frac{1}{r_{ij}} + \sum_{i>j} \epsilon_{ij} \left( \frac{r_{ij}}{r_{ij}^6} - 3 \left( \frac{r_{ij}}{r_{ij}^3} \right)^6 \right).
\]

The indices \(i\) and \(j\) run over all atoms types differentiated by the force field for that contribution to the potential energy, namely the real atoms F, C, O and H for the systems considered.

The partial charges in Table 6 indicate that no dipolar moments are allowed either on the symmetric molecules CH₄ or CO₂, while the polymer will bear one locally along the bisector of an –CH₂-CF₂–CH₂– angle. An attractive dipole-monopole contribution may hence involve O atoms from CO₂.

More significantly, the depths of pairwise 9-6 Lennard-Jones interactions in Table 6 show that O/C and O/F attractions are the strongest, so that a CO₂ molecule will be by far more attracted by PVDF than a CH₄. The much higher solubility of CO₂ in PVDF would then simply result from the large polarizability of the oxygen atom, which is the origin of the large \(\epsilon_{ij}\). Accordingly, the enthalpy of solubilization of CO₂ in PVDF must be higher (more negative) than that of CH₄, and as a result of the principle of Le Chatelier, the ratio of solubilities \(S\,\text{CO}_2/S\,\text{CH}_4\) should decrease as temperature increase. This latter tendency has been effectively observed in our simulations, as shown in Table 3. The temperature dependance of experimental solubilities of pure CO₂ in PVDF interpreted as an Arrhenian behavior provides an estimate of the molar enthalpy of solubilization close to \(-4.4\) kcal·mol⁻¹. This figure is also consistent with the dominance of dispersion forces.
CONCLUSIONS

We have presented the results of a study aiming at the prediction of solubilities of gases in amorphous polymers by molecular simulation. We have developed a protocol to build and prepare relevant atomistic models. We have selected the most suitable force field among those available to us, on a criterion of final density of the model amorphous cell. We have run quite a significant amount of very computer intensive simulations in order to produce statistically significant estimates of solubilities. We have compared different methods to evaluate solubilities.

The comparison with experiments is very encouraging, and lead us to conclude that the GCMC approach is the most precise and flexible, insofar as it allows for studying composite isotherms, and it is not limited in principle to small molecules. The WIMC method gives acceptable results and may be viewed as a degraded alternative, significantly less computer intensive than the GCMC, and useful when orders of magnitudes only need to be estimated. The TST method, although very fast, did not deliver reliable values for the system considered.

We provide a simple picture of the interactions governing the solubilization of CO₂ and CH₄ in PVDF: the more intense dispersion forces involving O atoms in CO₂ suffice to account for the very different solubilities of the two gases.

In the case of mixtures, simulations did not evidence any significant associative behavior of the host molecules.

REFERENCES

1 Accelrys Inc. (Formerly Molecular Simulations Inc.), 9685 Scranton Road, San Diego CA 92121-3752 http://www.accelrys.com

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