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Résumé — **Évaluation par simulation moléculaire des solubilités de CO$_2$ et CH$_4$ dans le PVDF : comparaison de diverses méthodes** — Cet article présente une comparaison des techniques de simulation moléculaire permettant d'évaluer les solubilités de CO$_2$, CH$_4$ 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 CO$_2$ et CH$_4$ 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 CO$_2$ and CH$_4$ Solubilities in PVDF by Molecular Simulation: A Comparison of Various Methods* — *Molecular simulation techniques were compared to evaluate the solubilities of CO$_2$ and CH$_4$ 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 CO$_2$ and CH$_4$ 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 Atomistic 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 CO_2 and CH_4. 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 microprocesseur 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 "Gsnet" and "Gsdif" 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):

$$
\begin{aligned}
E_{\text{Total}} = &\sum_b \left[K_2(b-b_0)^2 + K_3(b-b_0)^3 + K_4(b-b_0)^4 \right] \\
&+ \sum_\Theta \left[H_2(\Theta-\Theta_0)^2 + H_3(\Theta-\Theta_0)^3 + H_4(\Theta-\Theta_0)^4 \right] \\
&+ \sum_\Phi \left[V_1(1-\cos\Phi) + V_2(1-2\cos\Phi) + V_3(1-3\cos\Phi) \right] \\
&+ \sum_\chi K(\chi-\chi_0)^2 + \sum_b \sum_{b'} F_{bb'}(b-b_0)(b'-b'_0) \\
&+ \sum_\Theta \sum_{\Theta'} F_{\Theta\Theta'}(\Theta-\Theta_0)(\Theta'-\Theta'_0) + \sum_b \sum_\Theta F_{b\Theta}(b-b_0)(\Theta-\Theta_0) \\
&+ \sum_b \sum_\Phi (b-b_0) \left[\begin{array}{l} F_{b\Phi}{}^1(1-\cos\Phi) + F_{b\Phi}{}^2(1-2\cos\Phi) \\ + F_{b\Phi}{}^3(1-3\cos\Phi) \end{array} \right] \\
&+ \sum_\Phi \sum_\Theta \sum_{\Theta'} K_{\Phi\Theta\Theta'} \cos\Phi(\Theta-\Theta_0)(\Theta'-\Theta'_0) \\
&+ \sum_{i>j} \frac{q_i q_j}{\varepsilon_{ij} r_{ij}} + \sum_{i>j} \varepsilon_{ij} \left[2\left(\frac{r_{ij}^*}{r_{ij}}\right)^9 - 3\left(\frac{r_{ij}^*}{r_{ij}}\right)^6 \right]
\end{aligned}
\tag{1}
$$

In this expression, the last two terms account for inter-molecular 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) ε_i (depth of the van der Waals self-interaction potential well for atom i) and r^*_i (distance of maximum attraction between two atoms of type i).

2.3 Building PVDF Model Amorphous Cells

We have built the repeat-unit h–(CH_2-CF_2)–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 system, 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_f at T and P in order to allow the model system to reach equilibrium through contraction instead of expansion. Reaching a realistic d_f 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;

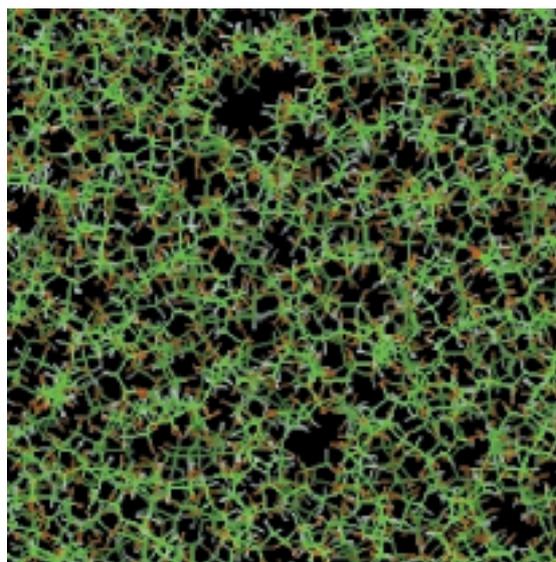
Figure 1

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 controlled thanks to the Andersen method, and *P* is controlled thanks to the Berendsen method. The latter restricts the cell unit-vectors to be orthonormal.

A front view of an equilibrated PVDF amorphous cell is shown on Figure 1. This image gives an idea of the type of free volume spatial distribution accessible to atomistic modelling.

2.4 Evaluation of Solubilities

2.4.1 The WIMC

This method [4] allows an evaluation of the Henry constant of a host molecule for a polymer matrix, *i.e.* the ratio solubility to pressure in the limit of vanishing pressure. A "ghost" host molecule is inserted at random in the matrix, and the resulting change in potential energy ΔU is computed. Notice that intermolecular interactions only will be taken into account. The configuration is accepted or rejected following the metropolis algorithm, whereby the Boltzmann factor $\exp(-\Delta U/kT)$ is compared to a random number generated in the interval [0-1]. The Henry constant is the limit to very large *N* of the serie defined in Equation (2):

$$H = \frac{V_{\text{cell}}}{kT} \frac{1}{N} \sum_{i=1,N} \exp(-\Delta U / kT) \qquad (2)$$

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

2.4.2 The TST

This method has been developed to account for solubilities and diffusivities of small molecules in a dense amorphous polymer [5]. It relies on the hypothesis that molecules diffuse in the polymer matrix from "sites" to "sites" (*i.e.* cavities of free volume) through thermally activated "hops", involving elastic local deformations of the matrix only. A grid is mapped onto the amorphous cell space, and each node of this grid is identified as a "site" with the probability density of presence $\rho(\mathbf{r})$ of a host molecule. In the theory, the elasticity factor $W(\{\Delta\})$ of the polymer matrix is explicitly related to the mean square displacement of individual atoms away from their equilibrium position, which can be evaluated for the given atomistic model thanks to a special molecular dynamics run. With these ingredients, an expression for the solubility in the limit of vanishing pressure is theoretically derived, giving another evaluation of the Henry constant.

2.4.3 The GCMC

This method evaluates the equilibrium solubility of a host molecule in a "porous" matrix through a Monte-Carlo simulation in the so-called grand canonical statistical ensemble, that is under fixed *T, V* and chemical potential (or fugacity *f* of the host). The method is fully atomistic, and not limited in principle to small molecules. The Monte-Carlo moves involved in our study are insertions, deletions, rotations and translations of a rigid host molecule (in principle, moves accounting for the flexibilities of the matrix and host can be also included in the process). Additions and deletions are accepted with the probabilities:

$$P_{\text{add}} = \min\left(\frac{PV}{(N+1)kT} \exp(-\Delta U / kT);1 \right) \qquad (3)$$

and:

$$P_{\text{delete}} = \min\left(\frac{NkT}{PV} \exp(-\Delta U / kT);1 \right) \qquad (4)$$

The average number $< N >$ of molecules inserted per unit-cell is a direct estimate of the solubility *S* through:

$$S = \frac{< N >}{P} \qquad (5)$$

And the Henry constant can be derived from:

$$H = \lim_{P->0} \frac{< N >}{P} \qquad (6)$$

According to the GCMC method, it is possible to reconstruct the full solubility isotherm, by varying the host fugacity step by step, at the expense of a sizeable amount of computing 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 necessary. 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 $d = 1.4$ g·cm^{-3} and PCFF was consistently better with $d = 1.61$ 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 bar and *T* = 298 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

Solubilities at 298 K and a fugacity of 5 bar
of pure solute. Solubilities expressed in cm³ (STP)·cm^{-3} bar^{-1}.
Averaged over ~10 PVDF cells; DP = 100. PCFF force field

	S CH$_4$	S CO$_2$	S CO$_2$/S CH$_4$
TST	1.46	6.7	4.6
WIMC	0.2	0.91	4.48
CGMC	0.22	0.88	3.89

3.3 Results at *f* = 40 Bar and *T* = 408 K, Pure Gases

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

TABLE 2

Solubilities at 408 K and a fugacity of 40 bar
of pure solute. Solubilities expressed in cm³ (STP)·cm^{-3} bar^{-1}.
Averaged over ~10 PVDF cells; DP = 100. PCFF force field

	S CH$_4$	S CO$_2$	S CO$_2$/S CH$_4$
TST	0.29	0.77	2.63
WIMC	0.07	0.11	1.6
GCMC	0.07	0.08	1.28

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 bar and *T* = 293 K, Mixture 50% CO₂ + 50% CH₄

A distinctive cabability 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

Comparison of molecular simulation results with experimental data:
solubilities S in the amorphous phase are expressed
in cm³ (STP)·cm^{-3} bar^{-1}.
A: desorption method [9]; B: direct gravimetric method [10]

Temperature (K)	408	298	293**
S CO$_2$ (expt. A)	0.57	1.7	n.d.
S CH$_4$ (expt.A)	0.1	n.d.	n.d.
S CO$_2$/S CH$_4$ (expt. A)	6.0	n.d.	n.d
S CH$_4$ (expt. B)	~0*	~0*	n.d.
S CO$_2$ (expt. B)	0.085*	0.613*	0.86*
S CO$_2$ (GCMC)	0.088	0.88	0.82
S CH$_4$ (GCMC)	0.07	0.22	0.06
S CO$_2$/S CH$_4$ (GCMC)	1.0	4.0	15.0

* Corrected for an Arrhenian temperature dependance, and for the experimental crystallinity of 39.8%.

** Mixtures CO₂ + CH₄. 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 dependant.

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 cm³ (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 CH_4 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 CO_2 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 CH_4 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 solubilities of CH_4 and CO_2 cannot be discriminated by the experimental setup used in [10]. Assuming CH_4 is insoluble in PVDF, we observe no significant differences for S CO_2 when CO_2 belongs to a mixture.

It is now possible to discuss the origin of the different behaviors of CO_2 and CH_4 with respect to PVDF in terms of molecular interactions: because the GCMC is not a model dependant 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):

$$E_{\text{Intermolecular}} = \sum_{i>j} \frac{q_i q_j}{\varepsilon_{ij} r_{ij}} + \sum_{i>j} \varepsilon_{ij} \left[2 \left(\frac{r_{ij}^*}{r_{ij}} \right)^9 - 3 \left(\frac{r_{ij}^*}{r_{ij}} \right)^6 \right]$$

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 CH_4 or CO_2, while the polymer will bear one locally along the bisector of an $-CH_2-CF_2-CH_2-$ angle. An attractive dipole-monopole contribution may hence involve O atoms from CO_2.

TABLE 4

Distances of maximum intermolecular attraction
for atom pairs as parametrized in PCFF (Å)

r^*_{ij}	PCFF			
	F	C	H	O
F	**3.200**	3.712	3.106	3.388
C	**3.712**	**4.010**	3.669	3.809
H	**3.106**	**3.669**	**2.995**	3.319
O	**3.388**	**3.809**	**3.319**	**3.535**

TABLE 5

Relative depths of pairwise potential wells as parametrized in PCFF

ε_{ij}	PCFF			
	F	C	H	O
F	**0.060**	0.046	0.034	0.057
C	**0.046**	**0.054**	0.023	0.053
H	**0.034**	**0.023**	**0.020**	0.031
O	**0.057**	**0.053**	**0.031**	**0.060**

TABLE 6

Partial charges as assigned in PCFF (in electronic units)

C in H–C–H (PVDF)	–0.106
C in H–C-H (CH_4)	–0.212
C in O–C–O	0.24
C in F–C–F	0.5
F	–0.25
H	0.053
O	–0.12

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 CO_2 molecule will be by far more attracted by PVDF than a CH_4. The much higher solubility of CO_2 in PVDF would then simply result from the large polarizability of the oxygen ***atom***, which is the origin of the large ε_{ij}. Accordingly, the enthalpy of solubilization of CO_2 in PVDF must be higher (more negative) than that of CH_4, and as a result of the principle of Le Chatelier, the ratio of solubilities S CO_2/S 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 CO_2 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 compute 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 CO_2 and CH_4 in PVDF: the more intense dispersion forces involving O atoms in CO_2 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.

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