

COSMO-RS PREDICTING THERMODYNAMIC PROPERTIES IN POLYMERS

Whitepaper

COSMO-RS is a thermodynamic theory for liquid phases. However, under the assumption that polymers can be treated as solutions consisting of monomers or of oligomers with a small number of repeat units, COSMO-RS becomes a useful tool for the prediction of thermodynamic properties in polymers. This article summarizes some results concerning the computation of vapor-liquid and gas-liquid equilibria (i.e. gas solubilities) in different polymers and partition coefficients between polymer and solvent phase. Predictions for vapor-liquid equilibria and for partition coefficients can be improved by incorporation of free volume effects. It is demonstrated that a high predictive accuracy is obtained if the polymer is sufficiently characterized e.g. by its density and its crystallinity. The approach is currently limited to small and medium sized solutes and to linear, i.e. non-cross-linked polymers without any significant swelling.

Figure 1

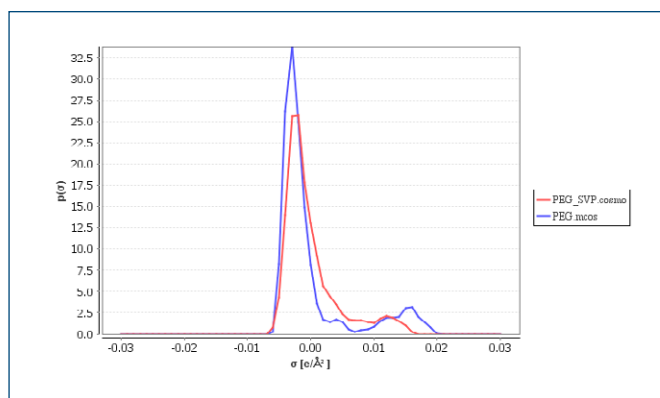


Figure 1: Two alternative COSMO-RS polymer representations of polyethyleneglycol (PEG) and the respective weight strings (a), (b) and σ -profiles of those representations (c).

Weight string based polymer representations can be easily constructed using the COSMOthermX graphical user-interface. Internally, the molecular weight and the COSMO volumes are modified according to the specified weights by COSMOtherm. Usually it is sufficient to use trimers, i.e. three repeat units capped with a suitable functional group. Currently, the weight string approach does not allow for taking more than one conformer into account.

Co-polymers can be obtained either by explicit construction of one single COSMO file containing both repeat units in their respective proportion, or by using a mixture of several separate homopolymers. The latter approach is somewhat more flexible as it allows for varying the composition of the co-polymer.

Please note, that another approach for representing polymers is used by COSMOquick^[14]. COSMOquick is able to instantaneously generate σ -profile from a 2D molecular topology, e.g. a SMILES string, by using a large database containing quantum-chemically pre-computed molecules. It allows for the construction of polymers by using SMILES strings which are end-capped by marker atoms, e.g. a halide atom. An example for polyethyleneglycol would be the SMILES string "ICOCI" or alternatively "ICCOL". For the construction of the so-called meta-cosmo file (.mcos file) from the fragment database (for details see the COSMOquick user guide) a ring closure is assumed at the position of the marker atoms and the final polymer representation corresponds to an infinite cyclic arrangement.

Within COSMO-RS, the combinatorial (non-ideal entropic) contribution to the chemical potential has been developed for molecules of small and moderate size. Therefore it is usually recommended to be switched off (COSMOtherm keyword combi) as it is not well suited for macromolecules.

Free volume effects play an important role for polymer solutions because small molecules usually have a high amount of free volume, which is significantly reduced upon mixing with the polymer. The free volume may be defined as the difference between the molar volume v_i and the molar hard core volume v_i^* . The hard

core volume may be computed either from van der Waals volumes or from COSMO volumes. Elbro and co-workers proposed a simple modification of the excess free energy, which closely resembles the Flory-Huggins combinatorial contribution^[9]:

$$(1) \quad G^{comb, fv} = RT \sum x_i \ln \left(\frac{\phi_i^{fv}}{x_i} \right)$$

ϕ_i^{fv} is the free volume fraction of compound i with mole fraction x_i . Here, the mole fraction and hard core volume v_i^* refer to the repeat unit of the pseudo liquid polymer.

$$(2) \quad \phi_i^{fv} = \frac{x_i (v_i - v_i^*)}{\sum_j x_j (v_j - v_j^*)}$$

This finally leads to the following additional contribution for the activity coefficient:

$$(3) \quad \ln \gamma_i^{fv} = \ln \left(\frac{\phi_i^{fv}}{x_i'} \right) + 1 - \frac{\phi_i^{fv}}{x_i'}$$

With x_i' now being the mole fraction with respect to the polymer chain. Thus, care should be taken to use the right definition of the mole fraction, which may be either referring to one mole of the repeat unit or, if the average molecular weight of the polymer is available, to one mole of polymer. As the molecular weight of the polymer is often either not known or not well defined, one often works with weight fraction based quantities for polymer solutions. The weight fraction based activity coefficient Ω can be obtained from the mole fraction based activity coefficient γ at small x_i according to:

$$(4) \quad \Omega_i = \frac{a_i}{w_i} \approx \gamma_i \frac{M_{polymer}}{M_i} \quad \text{with} \quad w_i \approx \frac{x_i M_i}{M_{polymer}}$$

Technically it is necessary to have the density for each solute and the polymer available, either experimentally or from a QSPR estimation. In the following the slightly larger COSMO volumes have been taken as hard core volumes and molar volumes have been obtained using densities from experiment. Interestingly, it was found that the Elbro term with Bondi van der Waals volumes scaled by a factor of 1.2 resulted in improved results as compared to the original volumes^[10]. Furthermore, in the same study the Elbro free volume correction has been reported to be superior to other free volume approaches, as the one of Oishi and Prausnitz for example. Pappa and co-workers compared the Elbro free volume correction with the combinatorial term of Zhong and Masuoka and concluded that the first is being superior^[11]. All in all, there seems to be a consensus that among the possible entropic correction the Elbro free volume term is the most favorable one^{[6][10][11]}. Consequently, in this study the approach of Elbro together with COSMO volumes was applied.

The following results have been generated with a recent COSMOtherm release^[12] and the respective COSMO-RS parameterizations BP_TZVP_C30_1401.ctd (TZVP level of theory). Modifications due to combinatorial terms and crystallinity have been computed subsequently on top of the COSMOtherm results. Low energy conformations of the molecular structures have been obtained using the COSMOconf workflow.^[13]

PREDICTION OF VAPOR-LIQUID EQUILIBRIA

The vapor-liquid equilibrium data used for the evaluation has been taken from the Polymer Solution Data Collection^[7]. Here, activities of the solutes have been obtained mostly by partial vapor pressure measurements of the mixture as compared to the pure substance vapor pressure with small corrections made due to the non-ideal character of the vapor.

In 33 out of the 38 investigated systems an improvement of the predicted activities is obtained by taking into account the simple free volume contribution from Elbro and co-workers (Figure 2 and Table 1). However, there are also a few examples where the pure COSMOtherm and the free volume augmented computations deviate significantly from the experiment. The two most extreme cases appear for polyvinylacetate (PVAC) with water and with 2-methylheptane (iso-octane) respectively, see Figure 3. It seems that the solubility of water in PVAC is completely overestimated for the COSMOtherm-FV calculations whereas the opposite is true for

the solubility of 2-methylheptane in PVAC. The pure COSMOtherm computations both underestimate the solubilities. A possible explanation for a solubility overestimation for water in PVAC could be the chosen experimental setup^[15]. The polymer sample was leached in water several weeks at elevated temperature and then dried prior to the solubility experiment. An incomplete drying process could have caused a limited uptake of additional water in PVAC and thus would result in a decreased solubility. Currently we do not have a better explanation at hand for this particular discrepancy. The case of 2-methylheptane remains particularly puzzling, as other solutes are well described within PVAC, and also alkanes seem to behave well in other polymers. Moreover, experimentally determined activities of alkanes in ethylacetate^[16] as a reference system for PVAC are all somewhat higher than those computed by the standard COSMOtherm. This raises some doubts on the reliability of the experimental data of the 2-methylheptane / PVAC system. A summary over all calculations is presented in Table 1.

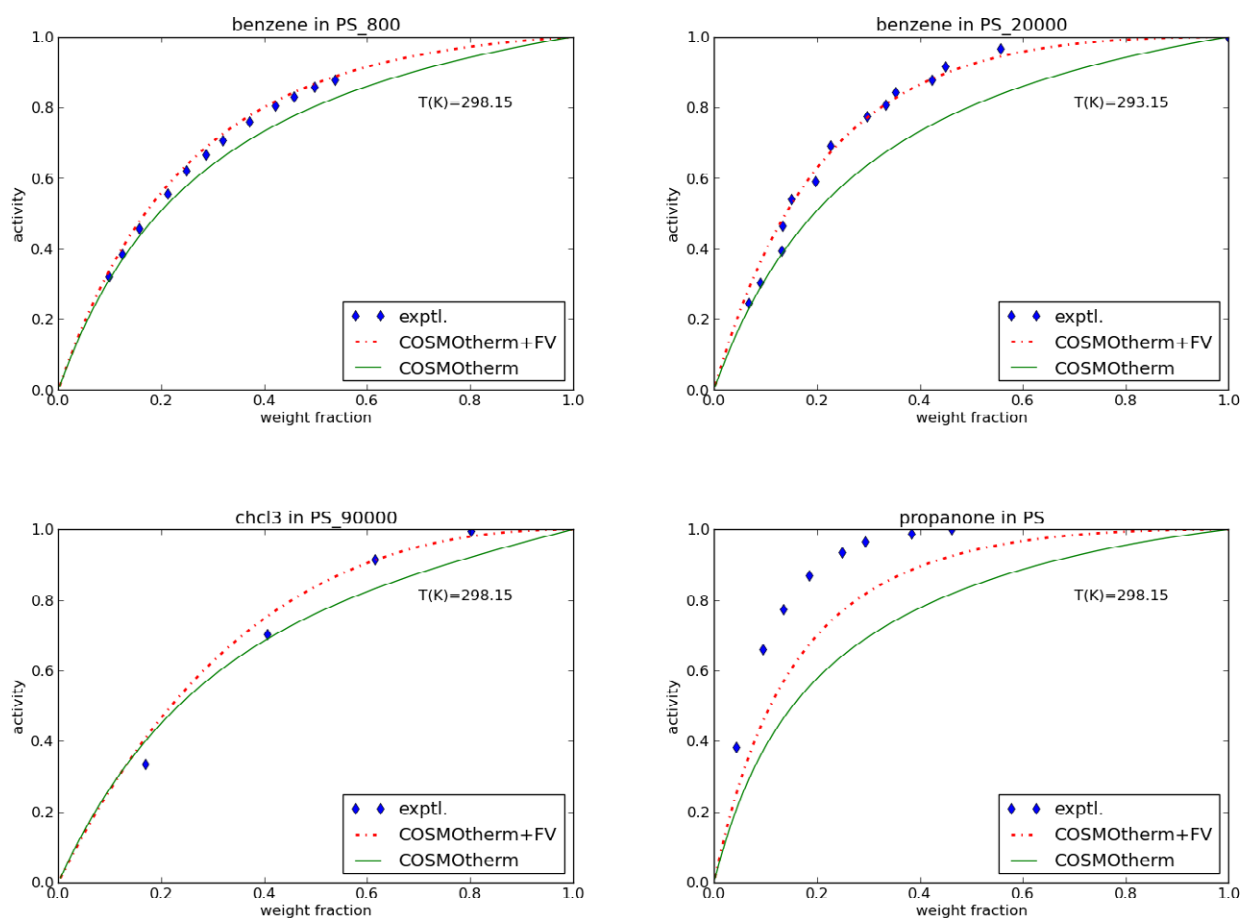


Figure 2: Activities for some solvent – polymer systems as predicted by COSMOtherm and comparison with experiment. Free volume effects are taken into account by the Elbro combinatorial contribution (red line). COSMOtherm results without combinatorial contribution to the chemical potential are also given (green line). Shown polymers are polystyrene with MW=800 g/mol, MW=20000 g/mol and MW=90000 g/mol, respectively (PS_800, PS_20000 and PS_90000).

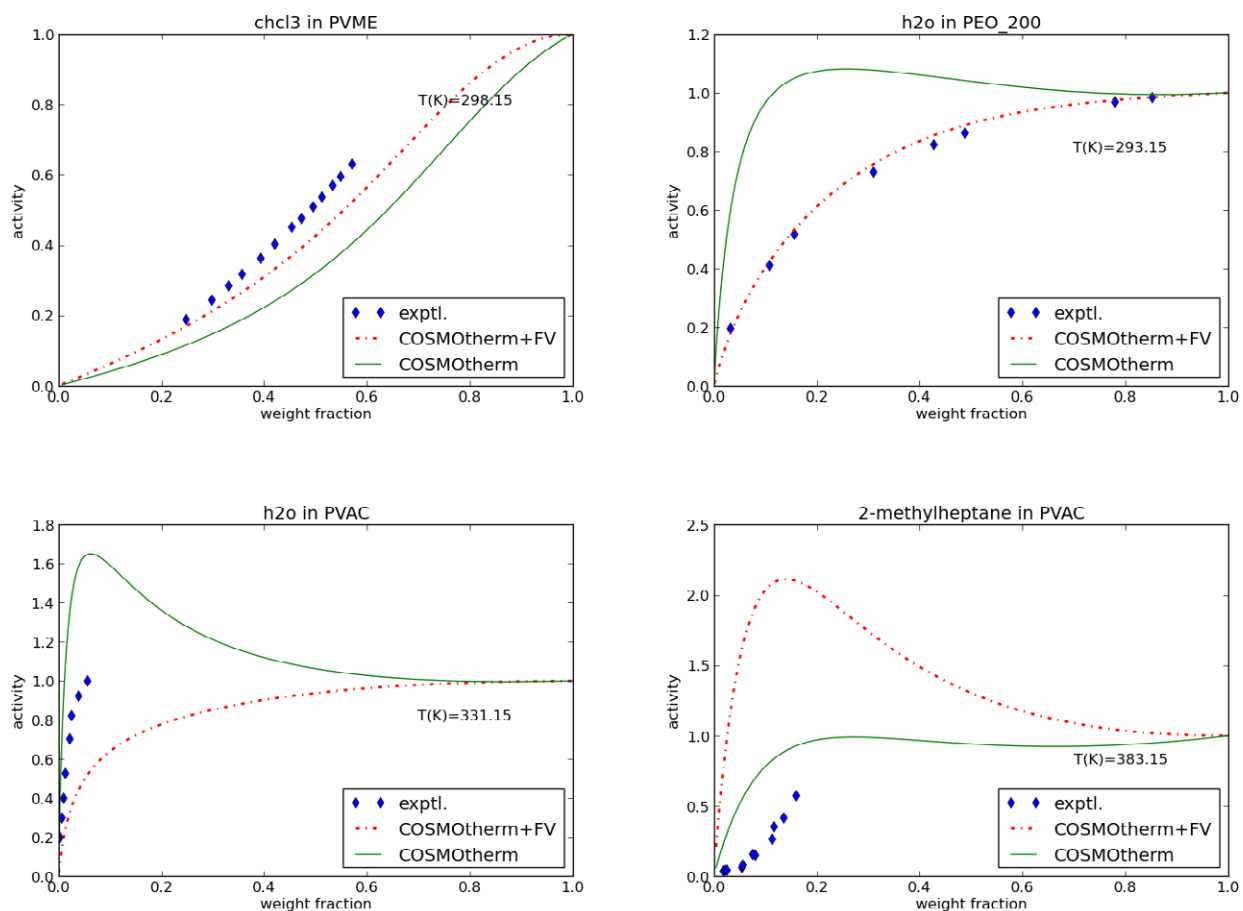


Figure 3: Activities for some solvent – polymer systems as predicted by COSMOtherm and comparison with experiment. Free volume effects are taken into account by the Elbro combinatorial contribution (red line). COSMOtherm results without combinatorial contribution to the chemical potential are also given (green line). Shown polymers are polyvinylmethylether (PVME), polyethylene oxide with 200 g/mol (PEO_200) and polyvinylacetate (PVAC).

polymer	solute	T(K)	FV,solvent	FV,solute	RMSE	CT, no comb. RMSE	CT + combinatorial RMSE	CT + FH RMSE
EVA	cyclohexane	383	37.9%	29.6%	0.03	0.07	0.06	0.06
EVA	2-methylheptane	383	37.9%	29.9%	0.08	0.10	0.05	0.05
PE	ch3br	273	16.3%	27.2%	0.45	0.46	0.29	0.29
PE	benzene	273	16.3%	25.7%	0.47	0.47	0.29	0.29
PE	hexane	273	16.3%	32.8%	0.56	0.56	0.44	0.44
PE	isobutene	273	16.3%	38.5%	0.41	0.41	0.35	0.35
Nitrocellulose	propanone	308	12.6%	30.1%	0.07	0.08	0.05	0.05
Nitrocellulose	methylacetate	308	12.6%	26.6%	0.07	0.08	0.05	0.05
Nitrocellulose	ethylacetate	293	12.6%	27.8%	0.23	0.24	0.21	0.21
PDMS	butanone	303	27.7%	28.1%	0.19	0.21	0.09	0.09
PEO	chcl3	298	7.4%	21.1%	0.20	0.20	0.17	0.17
PEO	h2o	293	15.9%	14.5%	0.35	0.20	0.04	0.04
PIP	p-xylene	298	18.2%	25.0%	0.28	0.30	0.13	0.13
PMMA	toluene	322	13.8%	25.8%	0.20	0.23	0.11	0.11
PMMA	butanone	322	13.8%	28.1%	0.20	0.24	0.15	0.15
PPO	methanol	298	21.0%	28.0%	0.06	0.07	0.03	0.03
PPO	benzene	333	21.0%	25.7%	0.14	0.16	0.01	0.01
PS	propanone	298	16.9%	30.1%	0.26	0.33	0.30	0.30
PS (Mn=20000)	benzene	293	16.9%	25.7%	0.11	0.15	0.09	0.09
PS (Mn=500000)	benzene	293	16.9%	25.7%	0.13	0.17	0.12	0.12
PS (Mn=800)	benzene	298	16.9%	25.7%	0.04	0.08	0.06	0.06
PS	chcl3	298	16.9%	21.1%	0.06	0.08	0.03	0.03
PVAC	benzene	303	16.9%	25.7%	0.14	0.16	0.05	0.05
PVAC	h2o	331	16.9%	14.5%	0.53	0.03	0.31	0.31
PVAC	2-methylheptane	383	16.9%	29.9%	0.43	0.41	0.95	0.95
PVAC	propanone	303	16.9%	30.1%	0.09	0.05	0.09	0.09
PVAC	propanol	303	16.9%	26.0%	0.21	0.25	0.22	0.22
PVAC	benzene	335	16.9%	25.7%	0.02	0.02	0.00	0.00
PVAC	vinylacetate	303	16.9%	26.4%	0.15	0.17	0.06	0.06
PVC	thf	298	13.1%	26.3%	0.23	0.24	0.09	0.09
PVC	toluene	316	13.1%	25.8%	0.22	0.23	0.11	0.11
PVME	chcl3	298	19.2%	21.1%	0.17	0.18	0.09	0.09
PVME	benzene	298	19.2%	25.7%	0.17	0.18	0.01	0.01
PVOH (Mn=14700)	h2o	303	7.8%	14.5%	0.07	0.17	0.21	0.21
PVOH (Mn=67000)	h2o	303	7.8%	14.5%	0.08	0.18	0.23	0.23
Polybutadiene	chcl3	298	20.6%	21.1%	0.09	0.11	0.03	0.03
Polybutadiene	nonane	353	20.6%	28.8%	0.38	0.38	0.22	0.22
celluloseacetate	ch2cl2	298	9.1%	22.0%	0.20	0.21	0.15	0.15
average			17.1%	25.6%	0.14	0.20	0.21	0.16

Table 1: Summary of COSMOtherm calculations on some data sets of the polymer solution data collection^[7]. For the comparison between experiment and prediction the root mean squared error (RMSE) from the solute activity is given, computed at n different weight fractions. The free volume of solvent and solute are given in percentage relative to the molar volume. RMSE values of COSMOtherm calculations using the Elbro term (CT+FV), without combinatorial term (CT, no comb.), with the default COSMOtherm combinatorial term (CT+comb.) and with the Flory-Huggins term are given (CT+ FH).

The results of Table 1 indicate that a clear improvement is obtained for polymer solutions by consideration of a polymer specific entropy change upon mixing. As a drawback a sufficiently accurate density of the polymer has to be specified, as well as the number average molecular weight M_n . The free volume term is considerably sensitive to small changes in the density, which in principle allows for example to differentiate between low density and high density polyethylene. The M_n is less important, as typically molecular weights $> 10,000$ g/mol do not influence results based on the Elbro free volume term anymore. Typical polymer molecular weights mostly influence the ideal entropic mixture contribution $RT \ln(x)$, which becomes almost zero except for very small solute-polymer weight fractions. Thus, using the free volume term most often raises the chemical potential, as overall free volume is lost in the mixture as compared to the pure solutes (see Table 1) and the $RT \ln(x)$ term becomes less negative.

POLYMER DENSITY ESTIMATION

As experimental determined densities of polymers are often not available it may be advantageous to use estimated values. Figure 4 plots the densities of polymers as obtained by the default COSMOtherm QSPR against experimental data. Using a simple linear regression to adapt these estimations for polymer solvents (and keeping the default QSPR for the solutes) and subsequent computations of activities on the dataset from the previous section leads to an overall RMSE = 0.16, as compared to an RMSE = 0.14 using experimental densities^[17]. It was not yet tried to improve this relation, which has been used just for the sake of simplicity, with some additional descriptors and more data points. Concerning the outlier in Figure 4, PTFE, its density seem to vary strongly, values from 2.2 g/cm³ (high density PTFE) to 1.55 g/cm³ (low density) are reported in the literature.^[17] Alternatively, a few other density models are available like the group contribution GCVOL method and the Tait equation^[11]. However, as the free volume contribution is very sensitive to small changes in the density, it is strongly recommended to use experimental data if available.

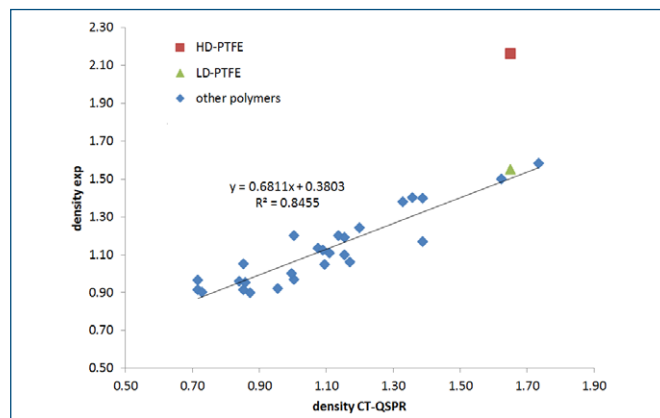


Figure 4: Polymer densities as predicted by the COSMOtherm QSPR model against experimental data. An outlier is polytetrafluoroethylene (PTFE), which however according to reference^[17] has a broad range of experimental densities, between its low-density (LD-PTFE) and high density variant (HD-PTFE).

PREDICTION OF SOLUBILITY COEFFICIENTS OF GASES AND SMALL MOLECULES (GAS-LIQUID EQUILIBRIA)

The solubility of gases in polymers is of interest for example for the development of polymeric membranes, barrier polymers or for polymer gas sensors. For this study experimental gas solubilities have been taken from the compilation of Pauly^[8]. As extension to an earlier work from one of us^[1], the aim of this study was to re-examine the data set with an actual implementation of COSMO-RS and also to include free volume effects, in order to get rid of the polymer-specific constant that had been necessary before. The gas solubility S is often given in the following or related units:

$$(5) \text{ Units of } S: \frac{\text{cm}^3 \{STP\}}{\text{cm}^3 \text{Pa}}$$

i.e. the dissolved volume of gas at standard temperature and pressure (STP: 273.15K and 1.013 10⁵ Pa) in cm³ in volume of polymer in cm³. Please note, that unfortunately there is a typo in the introductory part of the Pauly data collection concerning the units of permeability which directly translates into wrong units for the solubility (cm² instead of cm³ in the numerator of S). The solubility S as defined according to equation⁽⁵⁾ equals the inverse of the Henry's law constant. Within COSMOtherm the Henry's law constant is computed in the "COSMO-RS framework", i.e. a reference state corresponding to mole fractions gas per mole fractions solvent. Therefore, it has to be converted to the right reference state (called the "molar framework" within COSMOtherm) first, before it can be used to obtain S by simple inversion:

$$(6) \quad S \left[\frac{\text{cm}^3}{\text{cm}^3 \text{bar}} \right] = \frac{1}{H \left[\frac{x \text{ bar}}{x} \right]} \frac{\phi_{\text{solvent}} \left[\frac{\text{g}}{\text{cm}^3} \right]}{MW_{\text{solvent}} \left[\frac{\text{g}}{\text{mol}} \right]} V_{\text{ig}} \left[\frac{\text{l}}{\text{mol}} \right] * 1000$$

Here, ρ_{solvent} is the density of the polymer, MW_{solvent} is the molecular weight of the polymer solvent, and H is the Henry constant in the COSMO-RS reference framework. Most of the experimental gas solubilities of the Pauly data set have been measure indirectly, i.e. by measuring the permeability P and the diffusivity D , according to $S = P/D$, which is possibly less reliable than a direct measurement of S ^[18]. The Henry law constant H for compound i in solvent S is given by (see also the COSMOtherm manual):

$$(7) \quad H_s^i = \exp \left(\frac{\mu_s^i - \mu_{\text{IG}}^i}{RT} \right) = \ln \gamma_s^i p_{\text{vap}}^{i, \text{IG}}$$

Whereas μ_s^i and μ_{IG}^i are the chemical potential of compound i in solvent S and in the gas phase, assuming ideal gas behavior, respectively. Furthermore, γ_s^i and $p_{\text{vap}}^{i, \text{IG}}$ are the activity coefficient of solute i in solvent S and the pure compound vapor pressure of i assuming ideal gas behavior. In the following the

experimental vapor pressures have been used, in combination with the COSMOtherm computed activity coefficients. To estimate vapor pressures for small gases with critical temperatures below 298K, either extrapolation via Wagner coefficients has been done, or if those coefficients were not available, an extrapolation with COSMOtherm has been carried out.

The results of the gas solubility predictions are summarized for 15 different polymers in Table 2 and Figure 4. Table 2 shows three different COSMOtherm runs, using no combinatorial contribution at all, the Elbro free volume and the Flory-Huggins term. The combinatorial contribution does not have a significant influence on the outcome, an overall squared correlation coefficient R^2 of about 0.8 and a RMSE of $\log_{10}(S)$ of about 0.6 is obtained

for any of the approaches chosen. For the polymers HDPE, LDPE and PTFE there was initially a systematic shift in the predicted solubilities. This shift can be explained by the fact that these polymers are semicrystalline, i.e. containing a significant crystalline fraction, and assuming that sorption takes place only in the amorphous and not in the crystalline region. The crystalline fraction α of a polymer can be estimated by its actual density, if the density of the crystalline and the amorphous region are known, according to:

$$(8) \quad \alpha = \frac{\rho_{cryst}(\rho - \rho_{amorph})}{\rho(\rho_{cryst} - \rho_{amorph})}$$

polymer	n	CT, no comb. RMSE	R ²	CT + FV RMSE	R ²	CT + FH RMSE	R ²
Ethylcellulose	11	0.69	0.86	0.63	0.90	0.64	0.90
HDPE	10	0.67	0.59	0.68	0.59	0.68	0.60
Nitrocellulose	8	0.62	0.80	0.51	0.93	0.50	0.94
PEMA	6	0.39	0.93	0.79	0.93	0.79	0.92
Polyisopren	10	0.51	0.79	0.53	0.78	0.57	0.77
PTFE	10	1.02	0.53	1.03	0.53	1.02	0.51
PVC	7	0.69	0.76	0.90	0.78	0.89	0.78
LDPE	11	0.65	0.68	0.66	0.68	0.68	0.67
Polychloropren	6	0.56	0.79	0.43	0.92	0.40	0.93
PDMS	4	0.90	0.51	0.90	0.51	0.90	0.51
PODP	2	1.07	1.00	0.87	1.00	0.78	1.00
Polybutadiene	4	0.52	0.91	0.51	0.91	0.49	0.91
Polydimethylbutadiene	4	0.51	0.93	0.50	0.93	0.45	0.93
Polyvinylbenzoate	4	0.40	0.92	0.39	0.93	0.34	0.95
PET(40% cryst.)	4	0.39	0.82	0.37	0.84	0.29	0.91
PET(amorphous)	4	0.31	0.86	0.29	0.87	0.20	0.94
average		0.62	0.79	0.62	0.81	0.60	0.82

Table 2: Computed gas solubilities using no combinatorial contribution (CT,no comb.), using a free volume term (CT+FV) and the Flory-Huggins term (CT+FH) and their comparison with experiment^[8]. Results for HDPE, LDPE and PTFE have been corrected assuming a crystalline fraction α (see Table 3). The number of gas solutes is given by n. RMSE and R^2 are given with respect to the logarithmic solubility $\log_{10}(S)$, with S given in $[\text{cm}^3/\text{cm}^3\text{bar}]$.

polymer	$\rho[\text{g}/\text{cm}^3]$	$\rho_{cryst.}$	$\rho_{amorph.}$	α_{exp}	α_{exp}
LDPE	0.91	1.00	0.85	0.47	0.63
HDPE	0.96	1.00	0.85	0.79	0.91
PTFE	2.20	2.35	2.00	0.61	0.73

Table 3: Crystalline fractions α as computed from the gas solubility S for the semicrystalline polymers LDPE, HDPE and PTFE. Experimental values for α have been obtained using the known density, and the densities of the amorphous and the crystalline state according to equation^[8].

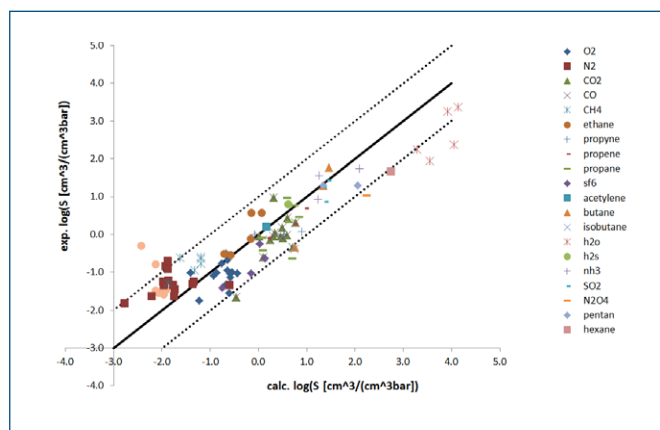


Figure 5: Predicted versus experimental gas solubilities in different polymers. Results for HDPE, LDPE and PTFE have been corrected assuming a crystalline fraction α (see Table 3). COSMOtherm results have been modified by using the free volume combinatorial contribution.

Concerning PET, separate experimental data for the amorphous and the semicrystalline polymer was given. Figure 5 shows that there are some outliers at either end of the solubility spectrum due to H_2 and to H_2O . The strong outliers for H_2 in PTFE and LDPE, which have been corrected for semicrystallinity, could be due to the fact that hydrogen as opposite to the other larger solutes is partially soluble also in the crystalline regions of those polymers. A possible explanation for the overestimation of the solubility of water is the fact that the constraints resulting from the polymer structure are suppressing the local structure formation required for the efficient solvation of a water molecule with its four strong interaction sites. Indeed, the polymers for which the solubility of water is overestimated have glass transitions above room temperature (PEMA, PVC, PODP, Ethylcellulose). Except for Nitrocellulose, where the overestimation is smallest, which has a glass transition below room temperature.^[17]

Taking the free volume effect into account does not influence the gas solubility results significantly. Most of the gases have a comparatively high liquid solubility within the polymers of this study, resulting in a free volume fraction ϕ^F_i close to one. Furthermore, the computed $\log(S)$ values have a significant contribution originating from the compound vapor pressure, i.e. mitigating any corrections made to the liquid phase.

Please note, that using COSMOtherm derived vapor pressure instead of experimental ones gave correlations of similar quality. However this lead to a somewhat worse RMSE, as for small gas molecules the predicted vapor pressure data seems to be systematically high.

PREDICTION OF PARTITION COEFFICIENTS

Partition coefficients $\log_{10}(P)$ between a polymer phase and a solvent are relevant for drug formulation and for plastic packaging materials for example. The partition coefficient may be computed according to:

(9)

$$\log_{10}(P_{poly,X}^i) = \left(\frac{\mu_X^i - \mu_{poly}^i}{RT \ln(10)} \right) + \log_{10} \left(\frac{V_{m,poly}}{V_{m,X}} \right) + \log_{10}(1.0 - \alpha)$$

Where μ_X^i and μ_{poly}^i are the pseudo chemical potentials of solute i in solvent X and in the polymer, V_m is the molar volume and α is the crystalline fraction in case the polymer is semicrystalline.

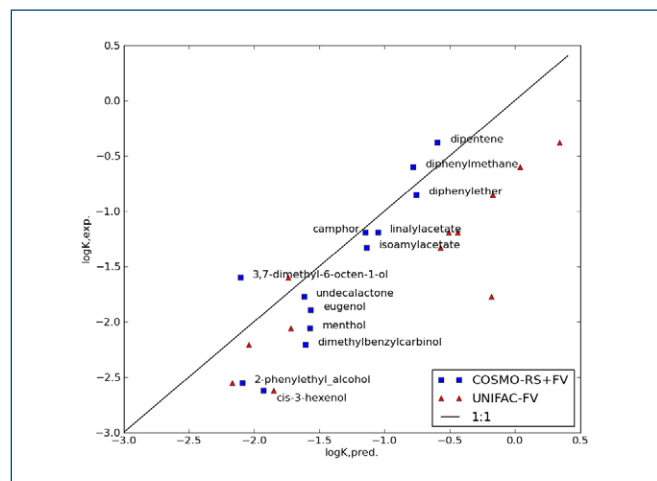


Figure 6: Experimental versus predicted partition coefficients for some fragrances between PE and ethanol as computed by COSMOtherm. Experimental data and UNIFAC-FV data has been taken from Reference^[19].

Experimental and UNIFAC-FV data for polyethylene-ethanol partitioning coefficients have been taken from Reference^[19]. Taking into account the Elbro free volume term and $\alpha = 0.63$ for LDPE as determined from the gas solubility calculations, the COSMOtherm prediction yield RMSE = 0.34 and $R^2 = 0.80$, compared to UNIFAC-FV with RMSE = 0.77 and $R^2 = 0.66$, see also Reference^[19].

Another data set containing polymer-water partition coefficients has been extracted from the work of Gasslander et al.^[20]. They have investigated the partitioning of molecules covering a broad range of polarity for the polymers polyethylene, polypropylene and polyethylene-co-butyl acrylate (17w% butylacrylate). Unfortunately, neither a density nor crystalline fraction of those polymers are specified in the paper. Thus the crystalline fraction α had to be treated as a fitting constant, which basically lowers the computed $\log P$ values by a constant shift, see equation⁽⁹⁾. The polymer-water partition coefficients have been determined indirectly via linear regression from liquid chromatographic retention times using acetonitrile, ethanol and isopropyl alcohol. Accordingly, no dissociation correction for acidic molecules in the water phase was carried out.

System	Level	α_{fit}^*	R^2	RMSE	slope	n
PE	CT	0.97(0.998)	0.87(0.97)	1.83(3.25)	0.42(0.45)	10(12)
PP	CT	0.99(0.999)	0.90(0.92)	1.09(3.47)	0.57(0.38)	8(10)
EBA	CT	0.96(0.998)	0.92(0.95)	1.11(2.99)	0.58(0.44)	10(12)
PE	CT+FV	0.67(0.91)	0.86(0.96)	1.13(1.76)	0.55(0.60)	10(12)
PP	CT+FV	0.79(0.97)	0.91(0.92)	0.55(2.02)	0.79(0.516)	8(10)
EBA	CT+FV	0.52(0.89)	0.95(0.95)	0.38(1.53)	0.89(0.62)	10(12)

Table 4: Summary of results of the dataset from reference^[20]. RMSE and R^2 have been determined with respect to the $\log_{10}(P)$ polymer, water. The slope of the linear regression and the number of data points n are also given. In parenthesis results including the 2 potential outliers bis(2-ethylhexyl)phthalate and octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoate

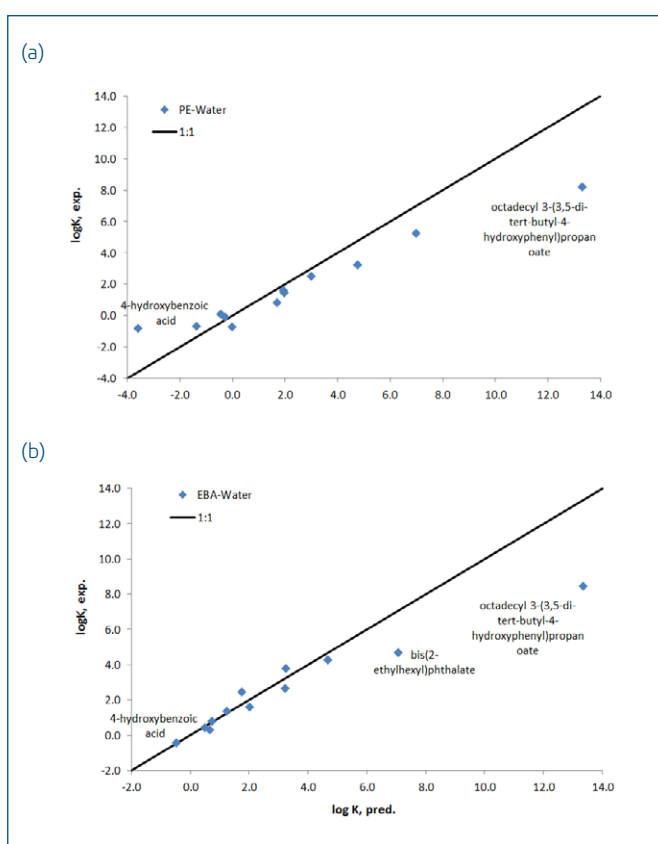


Figure 7: Experimental versus predicted partition coefficients between PE-water (a) and EBA-water (b). Experimental data has been taken from Reference^[20]. Predictions have been obtained using the free-volume combinatorial term and a (fitted) crystalline fraction of $\alpha=0.67$ (PE) and $\alpha=0.52$ (EBA).

Interestingly, as summarized in table 4, the regression slope of the predictions versus the experimental data is for all three polymers significantly below unity. This is partially due to the experimental data points belonging to the rather non-polar compounds, octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoate and bis(2-ethylhexyl)phthalate, having very high $\log K$ values, which are possibly out of range of what is reliably measurable. But, even excluding the two most extreme data points (see Table 4) the regression slope remains still somewhat low.

All in all, the experimental trend is predicted quite reliably, reflected by a squared correlation coefficient for all polymers of about 0.9, see also Figure 7. Furthermore, the results of table 4 clearly show that more consistent results are obtained if the free volume combinatorial term is included. The crystalline fraction, which has been used as a fitting constant, corresponds roughly to what can be expected from experience. The regression slope is somewhat higher, though still not unity, leading to a better coincidence with the experimental data and consequently a lower root mean squared error (RMSE).

solute	Log K, PE-water		Log K, PP-water		Log K, EBA-water	
	exp	CT + FV	exp	CT + FV	exp	CT + FV
4-hydroxybenzoic acid	-0.8	-3.6	-	-0.4	-0.4	-0.6
methyl-4-hydroxybenzoate	-0.7	-1.4	-	-1.5	0.4	0.3
4-methylbenzyl alcohol	-0.7	0.0	-0.6	-0.1	0.3	0.5
2-methylbenzoic acid	-0.1	-0.3	0.4	-0.4	0.8	0.8
propyl-4-hydroxybenzoate	0.1	-0.5	0.1	-0.5	1.4	1.1
diethyl phthalate	0.8	1.7	1.0	1.6	1.6	1.8
toluene	1.6	1.9	2.1	1.8	2.5	1.9
3,5-di-tert-butyl-4-hydroxyphenyl propanoic acid	1.5	2.0	2.2	1.9	2.7	3.3
2,4-di-tert-butylphenol	2.5	3.0	2.6	2.8	3.8	3.4
2,6-di-tert-butyl-4-methylphenol	3.3	4.8	3.9	4.6	4.3	4.9
bis(2-ethylhexyl)phthalate	5.3	7.0	4.5	6.9	4.7	7.1
octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propanoate	8.2	13.3	6.8	13.2	8.4	13.5

Table 5: Computed partition coefficients using the free volume combinatorial contribution for the experimental dataset from reference^[20].

CONCLUSION & OUTLOOK

In summary, it is feasible to make quantitative predictions using COSMO-RS theory for vapor/gas-liquid data and partition coefficients on systems containing polymers. In many cases consideration of free volume effects seems to improve the results as compared to the simple omission of the combinatorial term. However, this requires some additional information to be taken into account, i.e. the density of polymer and solute, the molecular weight and the crystallinity of the polymer. For the examined data it was sufficient to estimate the free volume simply based on the computed COSMO volumes. Sometimes, the study of polymer systems is hampered by the fact that experimental conditions are not specified with sufficient accuracy. Then, those missing parameters have to be fitted using the remaining experimental information.

Most of the investigated polymer systems were of a rather simple chemical structure, furthermore, crosslinking and polymer swelling effects were not examined so far. It remains to be shown whether such effects, which will play an important role in many practical applications, can be incorporated into COSMO-RS calculations.

Furthermore, the solubility prediction for larger, e.g. drug-like, solutes is not yet addressed here. Since having extremely long equilibration times in polymers, the experimental solubility data for such systems are often quite questionable.

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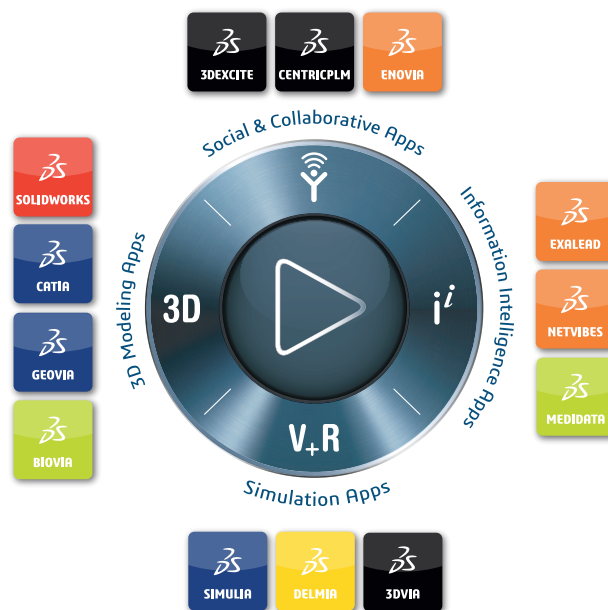
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