

the dispersive van-der-Waals interactions between the molecules (a^{disp}).

$$a^{\text{res}} = a - a^{\text{id}} = a^{\text{hc}} + a^{\text{disp}} \quad (1)$$

For PC-SAFT modeling, three parameters are required for characterizing each component in the system. A physically reasonable description is obtained using the segment number m^{seg} and the temperature-independent segment diameter σ to define the size of the molecule. An adequate representation of its dispersive, attractive interaction behavior is characterized by the dispersion-energy parameter u/k_B .

For a more-detailed description of the distinct contributions to the residual Helmholtz energy and the implementation of the pure-component parameters in the model equations the reader is referred to the original PC-SAFT publication of Gross and Sadowski [1].

An extension of the PC-SAFT to be used for copolymer systems was developed by Gross et al. [4] and was utilized within this work when copolymer systems were considered. A detailed description of the theory is renounced here and can be found in the original work.

For the modeling of multi-component systems the pure-component parameters of the involved substances are combined according to the van-der-Waals one-fluid theory [5]. In this way the mean segment number \bar{m}_{seg} is determined as a weighted average of the segment numbers of components i in the requested system.

$$\bar{m}^{\text{seg}} = \sum_i x_i m_i^{\text{seg}} \quad (2)$$

The combination of the segment diameters and the dispersion energies of a pair of unlike segments is done applying the Berthelot–Lorentz combining rules [6]. Here the segment diameters of component i and j are averaged arithmetically whereas the dispersion energy of the mixture is determined by a geometric mean.

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \quad (3)$$

$$\frac{u_{ij}}{k_B} = \sqrt{\frac{u_i}{k_B} \frac{u_j}{k_B} (1 - k_{ij})} \quad (4)$$

The parameter k_{ij} is called binary interaction parameter and is used as a correction factor for the dispersive interaction of a binary mixture consisting of components i and j . It is usually fitted to binary experimental data of the corresponding mixture.

3. Group-contribution method for polymer parameters: GCM-P

Inspired by the simple arithmetic and geometric form of the Berthelot–Lorentz combining rules, a group-contribution method for polymer parameters (GCM-P) was proposed in [2,3]. According to this, polymer parameters are calculated from group contributions using Eqs. (5)–(7).

$$\frac{u_i}{k_B} = \sum_{k=1}^{n_{\text{groups},i}} n_{k,i} \sqrt{\prod_{k=1}^{n_{\text{groups},i}} \left(\frac{u_k}{k_B}\right)^{n_{k,i}}} \quad (5)$$

$$\sigma_i = \frac{\sum_{k=1}^{n_{\text{groups},i}} n_{k,i} \sigma_k}{\sum_{k=1}^{n_{\text{groups},i}} n_{k,i}} \quad (6)$$

$$m_i^{\text{seg}} = \sum_{k=1}^{n_{\text{groups},i}} n_{k,i} m_k^{\text{seg}} \quad (7)$$

Here $n_{k,i}$ is the number of group k in polymer i . The sums and products are evaluated for all n_{groups} different groups in polymer i .

Parameterization of poly(olefins), poly(acrylates), poly(methacrylates) and further aromatic, oxygen- and silicon-based polymers was achieved using polymer groups —CH_3 , >CH_2 , >C(—O)—O— , >CH_{Ar} , $\text{>C}_{\text{Ar}}\text{—}$, —O— , >C=O , —OH and/or >Si(—) . A detailed description of the parameterization procedure for polymers as well as the GCM-P parameters are listed in corresponding tables of the previous publications [2,3].

However, since the GCM-P only provides pure-component polymer parameters, k_{ij} values were still fitted to binary experimental data.

4. Group contribution method for binary interaction parameters: GCM- k_{ij}

To obtain a fully-predictive method for polymer/solvent systems, in this work a second group-contribution method (GCM- k_{ij}) is proposed to estimate the binary interaction parameters k_{ij} . In fact, this is inspired by the calculation of the dispersion-energy parameter in a mixture based on the Berthelot–Lorentz combining rule (Eq. (8)). Using interaction parameters k_{ps} between polymer groups p and solvent groups s of a polymer/solvent system allows for the determination of the polymer/solvent binary parameter k_{ij} (derivation is given in Appendix A):

$$(1 - k_{ij}) = \frac{\left[\sum_{p=1}^{n_{\text{groups},i}} n_{p,i} * \sum_{s=1}^{n_{\text{groups},j}} n_{s,j} \right]}{\sqrt{\prod_{p=1}^{n_{\text{groups},i}} \prod_{s=1}^{n_{\text{groups},j}} (1 - k_{ps})^{n_{p,i} * n_{s,j}}}} \quad (8)$$

Here, binary interaction parameters k_{ps} between the different polymer and solvent groups are combined applying a geometric mixing rule.

For applying Eq. (8), the polymers were divided into same polymer groups as defined earlier [2,3]. For the GCM- k_{ij} determination, the solvent molecule is also divided into solvent-specific groups. However, the solvent groups were only used for the estimation of the k_{ij} whereas the pure-component solvent parameters were not determined from group contributions. Due to large solvent-parameter tables in the literature and extensively experimental solvent data for parameter fitting, there was no need for using a GCM for the solvent parameters.

The k_{ps} values for all investigated combinations of polymer groups and solvent groups within this work were determined by minimizing the deviations between the k_{ij} values obtained by Eq. (8) and the k_{ij} values that were obtained as a best manual fit to binary experimental polymer/solvent data.

Since poly(olefins) in solutions of linear alkanes and 1-alkenes were assumed to be most ideal with respect to their dispersive interactions and due to the best availability of experimental data for these systems, they were chosen as starting systems for the specification of the group contributions. Doing this, k_{ps} values were determined for —CH_3 , >CH_2 , $\text{>CH}_{2,\text{HDPE}}$, >C(—) and >C(—) polymer groups with —CH_3 , >CH_2 , >C(—) , $\text{=CH}_{2,\text{alkene}}$, =CH(—) alkene solvent groups. Maintaining this set of binary group contributions, poly(acrylates) and poly(methacrylates) dissolved in linear alkanes and 1-alkenes were studied next and group contributions were specified for solvent interactions with the —(C=O)—O— polymer group. For this purpose, (acrylate)- and (methacrylate)-based polymers were considered with up to four aliphatic polymer groups in the side-chain of the monomer unit, i.e. PBA and PBMA. In a subsequent step, poly(styrene) and its derivatives were considered. At the same time, the variety of considered solvents was extended toward cycloalkanes. Thus, new polymer/solvent group contributions were identified for the polymer groups >CH_{Ar} and >C_{Ar} , with solvent groups $\text{>CH}_{2,\text{Cyclo}}$ and $\text{>C(—)}_{\text{Cyclo}}$. Finally, new GCM- k_{ij} contributions were determined for solutions of

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