



New group contribution estimation of solvent activity in polymer solutions



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ABSTRACT

A new group contribution method (GCM) approach, based upon the combination of a thermodynamic model and molecular simulation (MS) is introduced. While other conventional GCMs require fitting with experimental data to determine group parameter values, proposed model calculates them directly using the pairwise interaction energy of functional groups (FG), obtained from MS. The solvent activities of a large variety of polymer solutions were estimated using the Helmholtz energy of mixing, based on the modified double lattice (MDL) model. For each polymer/solvent system, the interaction energy term within the Helmholtz energy expression is determined using the aforementioned group parameter derived from MS combined GCM (MS–GCM). From a number of polymer and solvent molecules, eleven FGs are defined. As considering FG connectivity, dummy atoms are introduced at the first adjacent positions in order to prevent impossible configurations during interaction energy calculation. The molecule disassembling method and dummy atom selection for each FG are carefully investigated. Newly proposed approach of MS–GCM could reduce the number of parameter much less than conventional GCMs but successfully predicted solvent activity. Its total deviation average of solvent activity estimation is 3.9%. Although it is little bit higher than previous work of Hu et al. but still remains in acceptable level.

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1. Introduction

Most polymer processes are based on the use of polymer solutions. Because 60–80% of the total cost in many processes is attributed to the separation step, understanding the phase equilibrium behavior of a given solution is important [1]. Vapor–liquid equilibrium (VLE) is one of the most important phenomena to be investigated by engineers during the early stage of process design. For engineers, in order to successfully design the process, they need practical data; unfortunately, this information is not always available. To overcome data deficiency, many predictive thermodynamic models have been introduced.

GCM is one of the most widely used methodologies developed to overcome the reliance on experimental data and to improve the prediction efficiency of models. The basic assumption of this approach is that the thermodynamic properties of molecules are determined by the sum of the contributions from each FG. Conversely, individual thermodynamic properties of a FG can be determined by regression to experimental data. Consequently, these group parameter values obtained from existing systems, as mentioned above, can be used to predict the behavior of unknown chemical compounds by re-structuring the FG accordingly.

Quasi-chemical theory of Guggenheim [2] was generalized to universal quasi-chemical (UNIQUAC) equation by Abrams and Prausnitz [3] through introduction of the local area fraction as the primary concentration variable. In UNIQUAC, applicable scope was extended from simplified molecules (monosized sphere) to mixtures of molecules consisting of various sizes and shapes. Fredenslund et al. [4] combined UNIQUAC with the FG concept and established UNIFAC that is most widely used mathematical expression of an activity coefficient treatment using GCM.

This method has been improved continuously; Oishi and Prausnitz [5] provided the free volume correction which suggested and extended the applicability of this method to polymer solutions. Hu et al. [6] presented a new GCM for the prediction of the VLE of polymer solutions. This model provides parameters for the cross-specific interaction energy from hydrogen bonding which are obtained by correlating the experimental data of vapor pressures with the infinite-dilution activity coefficients of a solvent. Conversely, parameters of the previous models were estimated from pure-component data. Later, Huh and Bae [7] combined GCM with MDL to reduce the number of group parameters from eighteen (the number used by Hu et al.) to six.

In addition to activity coefficient calculations, GCM has been developed for use in conjunction with an equation of state (EoS). In EoS–GE models, the excess Gibbs energy of mixing (GE) of the system is calculated with a predictive GCM such as UNIFAC. In this category, predictive Soave–Redlich–Kwong (PSRK) [8] is also one of

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the most widely used models, in which SRK-EoS [9] is combined with the existing parameter table of UNIFAC in order to calculate the attractive mixture parameter. Jaubert and Mutelet [10] developed PPR78 which is a GCM to estimate the temperature-dependent binary interaction parameters ($k_{ij}(T)$) for the widely used Peng–Robinson equation of state. Ahlers and Gmehling [11–13] published the volume translated Peng Robinson (VTPR) EoS which combines the Peng–Robinson EoS with UNIFAC to determine the adjustable parameters by fitting with the experimental vapor pressure data of the pure components.

Another widely used thermodynamic model accounting for the phase equilibria of liquid mixtures is the statistical associating fluid theory (SAFT) [14,15]. After first being combined with GCM by Lora et al. [16] SAFT has continued to adopt GCM and has been developed in to PC-SAFT [17], SAFT- γ [18,19] and GC-SAFT-VR [20,21].

All models, mentioned above, necessarily include interaction energy terms that account for contributions from component interactions. Because conventional GCMs determine these terms by regression to experimental data, if the necessary data is not available, the utilization of these models is restricted.

In this work, we calculated the interaction energy of FG pairs and the interaction parameter $\bar{\epsilon}$ of the thermodynamic equation by MS–GCM. $\bar{\epsilon}$ was substituted into the solvent activity formula that was derived from the Helmholtz energy of mixing, based on MDL.

To determine $\bar{\epsilon}$, simulation program calculate pair interaction between FGs. In case that one of component is polymer, it is more convenient to use repeat unit, rather than entire polymer chain. At the moment, steric hindrance caused by adjacent group must be taken into account. To prevent unreasonable configuration, Fan et al. [22] introduced dummy group concept for polymer analysis. In our study, dummy atom concept was expanded to FGs from component molecules. Detail of this method will be discussed at later part.

Years ago, Yang and Bae [23] published an MS technique that predicted the solvent activities of polymer solutions without fitting to experimental data. Differently from MS–GCM, this simulation method analyzed polymer solutions not with FG but with repeat unit. Meanwhile, how to define FGs with dummy is one of the most important part in MS–GCM, Yang did not consider alternative definition method of simulation components, but focused on applicability of interaction parameter from simulation to several thermodynamic models, such as Flory–Huggins lattice theory, generalized lattice–fluid model, and MDL. According to their work, it was proven that interaction parameter even without regression to experimental data could predict solvent activity successfully.

Yang's simulation method proposed a new approach; however its parameter values are not applicable for new systems, even where only one side chain of either polymer or solvent is changed. To get interaction parameter of new systems by this model, plant design engineers have to repeat the same computation process for each system. Therefore, this model proposed new method, but did not provide useful parameters for other systems.

Incorporating GCM concept into MS propose a new method to overcome this issue. Using the group parameter table obtained from MS–GCM, system designers can predict the solvent activity of new systems without additional MS operation.

Regarding estimation of solvent activity of polymer solution by GCM, Wibawa and Widyastuti [24] and Kuo et al. [25] individually proposed new group contribution methods. Wibawa introduced modified Entropic-Free-Volume model which combined combinatorial term from Entropic-Free-Volume model of Elbro et al. [26] and residual term that is derived from the enthalpy of mixing determined from solubility parameters. Kuo et al. proposed a method for predicting vapor–liquid and liquid–liquid equilibria

using COSMO-SAC [27–29] activity model. Where, screening charge distribution of polymers was obtained by quantum mechanical calculations. This approach that determines parameter values without regression to experimental data is similar to MS–GCM. In this model, however, oligomer which is bigger than repeat were used as a FG. It is farther from conventional GCM than simulation work of Yang and its usability of each parameter of polymer would be less than parameters from single carbon (C_1) based FGs.

To evaluate our proposed model, we compared the calculated solvent activity by MS–GCM with experimental data of various polymer/solvent systems. It was evaluated by polymer solutions with wide range of temperature and molecular weight of polybutadiene (PBD), polydimethylsiloxane (PDMS), polyethylene oxide (PEO), polyisobutylene (PIB), polystyrene (PS) and polyvinylacetate (PVAc). For more exact estimation, the FG definition method was studied in two different aspects beforehand: how to divide the molecules (in Section 6.2) and how to select the dummy atom elements (in Section 6.3).

2. Thermodynamic model of solvent activity

In general, the phase behavior of polymer/solvent system can be explained using lattice theory. Various lattice models have been developed over the years. Oh and Bae [30] defined a Helmholtz energy of mixing by using a form of the MDL (Eq. (1)), where N_r is the total number of lattice sites, k is the Boltzmann constant, r_i is the relative chain length and ϕ_i is the volume fraction of component i . Subscripts 1 and 2 refer to the solvent and polymer, respectively. The solvent chain length, r_1 , is fixed as one, and the relative chain length of polymer, r_2 is defined as a van der Waals volume [31,32] ratio of polymer to solvent.

For example, in PIB (MW = 2,250,000) in pentane solution, the r_2 , 28,237.1 was obtained by division of PIB volume (approximately $1,638,601\text{cm}^3/\text{mol}_{\text{PIB},(\text{CH}_2\text{C}(\text{CH}_3)_2)_n}$, $n = 40,093$) by pentane volume ($58.03\text{cm}^3/\text{mol}_{\text{pentane},\text{CH}_3(\text{CH}_2)_3\text{CH}_3}$). Where, volume of each component are summation of van der Waals volume, multiplied by number of FG. Van der Waals volume data, used in this model were presented in Table 1. When calculate polymer volume, volume of terminal FGs at both ends outside of repeat unit were neglected.

$$\frac{\Delta A}{N_r kT} = \left(\frac{\phi_1}{r_1}\right) \ln \phi_1 + \left(\frac{\phi_2}{r_2}\right) \ln \phi_2 + \chi_{OB} \phi_1 \phi_2 \quad (1)$$

Solvent activity experimental data [33] for model evaluations are expressed by a weight fraction base, so volume fractions in Eq. (1) must be converted to weight fractions by Eqs. (2) and (3). d_1

Table 1
van der Waals volume of FGs.

| Functional group | Volume (cm^3/mol) |
|--|-------------------------------------|
| C | 3.30 |
| CH | 6.80 |
| CH ₂ | 10.23 |
| CH ₃ | 13.67 |
| CO | 11.70 |
| –CH=CH– (cis/trans) | 24.30 |
| NH ₂ | 10.54 |
| O | 5.50 |
| Si | 16.60 |
| SiO | 22.10 |
| Si(CH ₃) ₂ | 42.20 |
| Cl | 11.60 |
| CH (aromatic, resonant) | 8.05 |
| C (aromatic, resonant) | 4.74 |
| Benzene (C ₆ H ₆) | 48.40 |
| Phenyl (C ₆ H ₅) | 43.30 |

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