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Estimation of second viral coefficient for polypropylene in organic solvents by computer simulation

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We present two new methods to estimate the value of the second viral coefficient for dilute polymer solutions. The first method utilizes the results of molecular dynamics simulation; the second one is based on the hybrid approach, which combines Monte-Carlo simulation with a numerical solution of the Ornstein-Zernike equation. The results show that both methods give the correct ascending arrangement of second viral coefficients for polypropylene solutions in organic solvents. The method based on molecular dynamics has a precision advantage, while the hybrid approach has better performance.

Keywords: polymer solutions, second viral coefficient, molecular dynamics, Monte-Carlo, Ornstein-Zernike equation.

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1. Introduction

The main problem with the theories claiming to describe equilibrium and dynamic properties of complex systems, such as „polymer+solvent“, polymer composites etc., consists in the need of correct accounting of the effects of volume interactions of polymer chain links with solvent molecules or inclusions at various scales. The central role in the study of polymer solutions belongs to the Flory-Huggings theory, where the volume interaction value is characterized by the value of the second virial coefficient. The most frequently used method to calculate the second virial coefficient in polymer solutions is semiphenomenological model UNIFAC (UNIQUAC Functional-group Activity Coefficient) [1,2]. Even though this method is successfully used to predict the phase equilibrium of complex systems, it will not always provide the accurate results and requires experimental verification. Besides, expanding the applications of UNIFAC method to describe the new materials requires high-precision experiments to determine the phenomenological coefficients.

The calculation of the second virial coefficient is of practical use to determine the mechanical resistance of polymer separators in lithium-ion batteries [3,4]. Experimental studies [5] have shown that depending on the used solvent, the polymer separator may swell significantly, losing its mechanical properties. In connection with the growth of interest in using new materials to manufacture separators, it becomes necessary to develop the method for selection of an ideal solvent.

To estimate the second virial coefficient, the computer modeling methods may be used. Despite the fact that there exist multiple papers to calculate the second virial coefficient by molecular dynamics (MD) method for homogeneous systems, the use of this method for the solutions is limited by „gas-liquid“ systems [6,7]. The promising approach is using hybrid circuit MC/RISM (Monte Carlo / Reference interaction site model) [8]. In this approach a single chain is modelled by Monte Carlo method, and the solvent at the same time is described in „simplified“ manner, using integral Ornstein–Zernicke equation (RISM theory equation). Influence of the solvent on the polymer chain is described by additional potential $\Delta\psi$, which is defined by self-agreed performance of Monte Carlo modelling and numerical solution to the integral equation. Even though this circuit is highly effective for computations, so far it has been used only within rather simple and coarse of polymer and solvent models.

This paper proposes two new methods to assess the volume interactions based on MD and MC/RISM approaches. The methods were tested on polypropylene solutions with various organic solvents (acetone, acetonitrile, cyclopentane, ethyl acetate and benzene). Previously in this paper [9] we studied the relaxation properties of polypropylene in these solutions.

2. Models and methods

To describe solvents and polymer molecules, power fields OPLS-ua and TraPPE-ua were used, where CH-groups are considered as single power centers. These power fields on the one hand provide for good accuracy of the description of experimental properties of substances, such as density and heat of vaporization, and on the other hand, are much more effective than full-atom models. It was assumed that the position of atoms inside the solvent molecule is fixed. Intermolecular interaction energy between the power centers of solvents consisted of Coulomb energy and Lennard-Jones potential (LD). The parameters of potentials were taken from papers [10–14]. LD interaction parameters for various power centers were calculated using the Lorentz–Berthelot consolidation rules.

To describe polypropylene molecules, a model TraPPE-ua [15] was used. The Hamiltonian of such model consists of LD potential, energy of covalent bonds, valent and torsion angles, and potential of „abnormal“ torsion angles, providing for building side CH_3-groups along one side of the polymer chain. The first of the methods we developed consists in using MD calculations and assessment of the volume interaction parameter using the following formula:

$$B_{\mathrm{MD}} = -2\pi \int_{0}^{\infty} g_{\mathrm{pp}}(r)\langle f_{\mathrm{M}}(r)\rangle r^2 dr,$$

$$f_{\mathrm{M}}(r) = \exp\left[-\frac{U_{\mathrm{pp}}(r)}{k_{\mathrm{B}}T}\right] - 1, \qquad (1)$$

where $g_{\mathrm{pp}}(r)$ — radial function of distribution „monomer-monomer“, $U_{\mathrm{pp}}(r)$ — potential energy of monomer interaction, $f_{\mathrm{M}}(r)$ — Mayer function.

Since in this model the potential energy of interaction is set not for monomers, but for the CH-groups that make them, the first step should be the calculation of the averaged Mayer function $\langle f_{\mathrm{M}}(r)\rangle$. For this purpose the preliminary MD modeling of the single chain in vacuum was performed. This modeling was performed in LAMMPS packet in a canonical assembly (NVT) at $T = 298.15\,\mathrm{K}$, the time increment was 0.25 fs, the total number of increments to calculate the radiation distribution functions was $1.6 \cdot 10^6$, the polypropylene chain consisted of 50 monomers. The value of pair potential energy of interaction of all power centers of polypropylene molecule and distance between them was recorded every 1000 increments. The average value of function $f_{\mathrm{M}}(r)$ was calculated by histogram method. The distance between monomers was the distance between CH_2 groups of polymer chain.

To calculate function $g_{\mathrm{pp}}(r)$, MD-modeling of a single chain was performed in a solution. The total number of solvent molecules was 5000 min. The box size and the number of solvent molecules were selected so that the concentration of solvent molecules corresponds to the table value at standard pressure. The time increment was 0.25 fs, the total number of increments, when the radial distribution functions were calculated, was equal to $4 \cdot 10^5$. Pair potentials „were cut“ at the distance of 20 Å, long-distance Coulomb interaction was taken into account via summation using Ewald method. To calculate the functions of radial distribution, standard LAMMPS means were used.

The second method proposed by us is based on the hybrid scheme MC/RISM, described in detail in paper [8]. To calculate the second virial coefficient, the following expression is used:

$$B_{\mathrm{MC}} = 2\pi \int \left[1 - \exp\left\{-\frac{U_{\mathrm{pp}}(r) + \Delta\psi(r)}{k_{\mathrm{B}}T}\right\}\right] r^2 dr, \qquad (2)$$

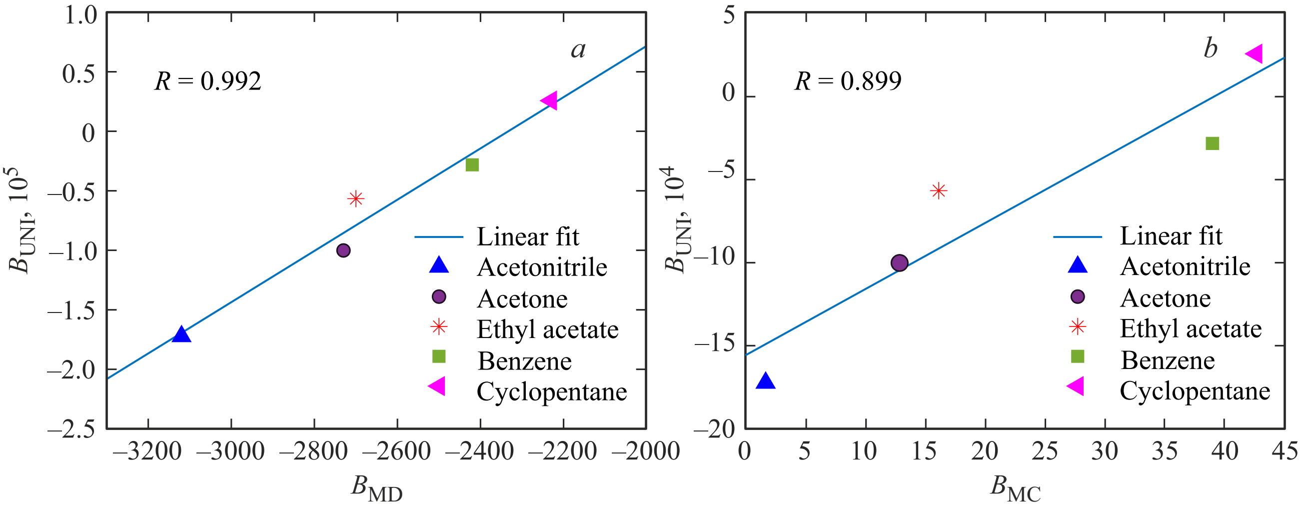
where $\Delta\psi(r)$ — addition to the potential produced as a result of MC/RISM-calculations and describing the effect of the solvent at the polymer. Monte Carlo modeling of a single chain was implemented in MATLAB packet. At each step of Monte Carlo a random node of the chain was chosen and shifted in space within the radius sphere 0.05 Å. Then the new configuration was accepted with the probability corresponding to the Metropolis standard criterion. The histogram of distribution of internodal distances in the chain was generated every 1000 steps of Monte Carlo. These calculations were repeated 500 times, and then the final function of the intramolecular distribution was calculated by averaging of these histograms.

The self-consistent solution of RISM equations was carried out according to the algorithm described in paper [8]. However, when correlation functions of the binary systems were determined, the convergence of this procedure fails due to a high number of sought functions (total $3 \cdot N_{\mathrm{s}}$ functions, where N_{s} — number of power centers in the solvent molecule). Therefore, to provide for convergence of the procedure for numerical solution, the mixing parameter τ was assigned a small value 0.001, and calculations were interrupted, when the average relative difference between the current and previous approximations of the function started increasing.

3. Discussion of results

To check the correct design of the developed methods, the parameters of volume interactions B_{MD} and B_{MC} calculated using formulas (1) and (2) were compared to the results of the calculations of the second virial coefficient using model UNIFAC-FV — B_{UNI}. Model UNIFAC-FV is an adequate verification method, since for the compounds in question the phenomenological coefficients have been well selected and verified.

The produced values B_{MD} and B_{MC} differ significantly from the results of method UNIFAC-FV. The cause for such deviations consists in the following: the polymer chain model we use contains „non-pair“ summands of potential energy, namely the energy of valence and torsion angles, which may not be taken into account in formulas (1) and (2). Nevertheless, one may assume that the contribution of these interactions hardly depends on the solvent. Then, if this assumption is correct, there must be correlation between the values of virial coefficients produced by methods UNIFAC-FV and MD. Indeed, if one builds dependences B_{UNI} on B_{MD} and B_{MC} (Figure) for various solvents, the produced points are aligned well in the linear dependence. At the same time all three methods provide the correct comparative characteristic of the volume interaction value in the solution. In other words, if solvents are located



Correlation of the values of the second virial coefficient produced by methods UNIFAC-FV (B_{UNI}) and *a*) of molecular dynamics (B_{MD}), *b*) MC/RISM (B_{MC}). The figures specify the value of linear correlation coefficient R.

in the ascending order of the produced virial coefficients, both methods provide the same row: acetonitrile, acetone, ethyl acetate, benzene and cyclopentane. Linear approximation in MC/RISM method has inferior agreement (coefficient of linear correlation $R = 0.899$), compared to MD method ($R = 0.992$). Nevertheless, despite lower accuracy compared to MD method, MC/RISM method has higher computational speed, since it uses simplified „language“ of intergral equations for description of solvents.

4. Conclusion

Compared to UNIFAC-FV method, both developed method correctly provide the comparative characteristic of the second virial coefficients for solutions of polypropylene with organic solvents. It is shown that there is a linear correlation between the results of the developed methods and UNIFAC-FV method, and therefore it is possible to assess the virial coefficient of polymer solution, knowing the virial coefficient for two other solutions of this polymer.

Conflict of interest

The authors declare that they have no conflict of interest.

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