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Pressure-volume-temperature and excess molar volume prediction of amorphous and crystallizable polymer blends by equation of state

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ABSTRACT

In this work the statistical mechanical equation of state was developed for volumetric properties of crystalline and amorphous polymer blends. The Ihm–Song–Mason equations of state (ISMEOS) based on temperature and density at melting point (T_m and ρ_m) as scaling constants were developed for crystalline polymers such as poly(propylene glycol) + poly(ethylene glycol)-200 (PPG + PEG-200), poly(ethylene glycol) methyl ether-300 (PEGME-350) + PEG-200 and PEGME-350 + PEG-600. Furthermore, for amorphous polymer blends containing poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) + polystyrene (PS) and PS + poly(vinylmethylether) (PVME), the density and surface tension at glass transition (ρ_g and γ_g) were used for estimation of second Virial coefficient. The calculation of second Virial coefficients (B_2), effective van der Waals co-volume (b) and correction factor (α) was required for judgment about applicability of this model. The obtained results by ISMEOS for crystalline and amorphous polymer blends were in good agreement with the experimental data with absolute average deviations of 0.84% and 1.04%, respectively.

1. Introduction

The quantitative description of dense polymer melts and blends is a problem of industrial and theoretical interest. As the processing of a large number of polymeric materials is frequently carried out in the molten state, it is important to estimate the pressure–volume–temperature properties and phase behavior of these materials accurately under conditions unavailable experimentally. This is essential in equipment design and process simulation. Existing empirical equations have been developed to predict the volumetric properties, such as the Tait equation [1]. In recent years, different theoretical equation of state (EOS) based on extensive pressure–volume–temperature (*pVT*) data of pure polymers [2–9], and against vapor–liquid equilibria and liquid–liquid equilibria of blend systems [10–12] has been developed. For example, Sato *et al.* [4] present a new group-contribution modified cell model EOS (GCMCM EOS) to predict *pVT* properties of polymer melts. Furthermore, if one specific volume datum at atmospheric pressure is used, the average prediction error of *pVT* by GCMCM EOS can be reduced to 0.27% for the homopolymers and 0.34% for the copolymers and blend polymers. Also, Papari *et al.* [5] employed Ihm–Song–Mason EOS (ISMEOS) for compressed pure polymeric fluids using two scaling constants both at the glass transition point. The average absolute deviation (AAD) between the calculated and the experimental densities for 421 data point of five polymers was around 0.6%. Besides, Hosseini *et al.* [7] demonstrated the modeling of the *pVT* properties of 14 melting polymers using simplified Yukawa hard-sphere-chain EOS plus first-order perturbation theory with overall AAD of the calculated specific volumes about 0.89%. Then, Yousefi and Karimi [8,9] successfully employed ISM and TM EOS using two scaling constants both at the melting point for high and low density pure polymer liquids over a wide range of temperatures and pressures.

This research focuses on the calculations of volumetric properties of some crystalline polymer blends such as poly(ethylene glycol) methyl ether(PEGME-350) + poly(ethylene glycol) PEG-200, PEGME-350 + PEG-600, poly(propylene glycol) (PPG) + poly(ethylene glycol) (PEG) and amorphous polymer blends contain poly(2,6-dimethyl-1,4-phenylene oxide)(PPO) + poly styrene (PS) and PS + poly(vinylmethylether) (PVME) at compressed states in the temperature range 298.15 K to 634.6 K and pressures to 200.0 MPa using modified Ihm–Song–Mason (ISM) equations of state [13]. Finally, the efficiency of this approach is compared with experimental data.

2. Theoretical Equation of State

2.1. ISM equation of state

Statistical mechanics provides us with the following equation, assuming a pair-wise additive central intermolecular potential [14],

$$\frac{p}{\rho kT} = 1-\left(\frac{2\pi\rho}{3kT}\right)\int_{0}^{\infty}\left(\frac{\partial u}{\partial r}\right)g(r)r^{3}\mathrm{d}r \qquad (1)$$

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where p is the pressure, ρ is the density, $g(r)$ is the pair distribution function and $\left(\frac{\partial u}{\partial r}\right)$ is the derivative of the intermolecular potential, $u(r)$, with respect to distance, r. Applying the Weeks–Chandler–Anderson division for the potential energy function [15], Ihm *et al.* [13] derived the following equation:

$$\frac{p}{\rho kT}=1+B_2\rho+\alpha\rho[G(b\rho)-1] \tag{2}$$

where B_2 is the second Virial coefficient, α is the repulsive contribution to the second Virial coefficient, $G(b\rho)$ is the average pair distribution function at contact for equivalent hard spheres, and b is the analog of the van der Waals covolume and can be calculated from α by the following equation:

$$b=\alpha+T\frac{\mathrm{d}\alpha}{\mathrm{d}T}. \tag{3}$$

All of the temperature-dependent parameters, B_2, α, and b, can be written in terms of the intermolecular pair potential in reference [16].

$$B_2=2\pi\int_0^\infty\left[1-\exp\left(-\frac{u}{kT}\right)\right]r^2\mathrm{d}r \tag{4}$$

$$\alpha=2\pi\int_0^{r_\mathrm{m}}\left[1-\exp\left(-\frac{u_0}{kT}\right)\right]r^2\mathrm{d}r \tag{5}$$

and

$$b=\frac{2}{3}\pi d^3=2\pi\int_0^{r_\mathrm{m}}\left[1-\left(1+\frac{u_0}{kT}\right)\exp\left(-\frac{u_0}{kT}\right)\right]r^2\mathrm{d}r \tag{6}$$

where d is the effective hard-sphere diameter and u_0 is the repulsive branch of u defined as [15]

$$u_0(r)=\left\{\begin{array}{ll}u(r)+\varepsilon, & r\le r_\mathrm{m}\\ 0, & r\ge r_\mathrm{m}\end{array}\right\} \tag{7}$$

where ε is the potential well-depth and r_m is the position of minimum in u.

Ihm *et al.* [13] used the Carnaham–Starling equation for $G(b\rho)$ [17] and performed a correction in Eq. (2) for the attractive forces to obtain

$$\frac{p}{\rho kT}=1-\frac{(\alpha-B_2)\rho}{1+0.22\lambda b\rho}+\frac{\alpha\rho}{1-\lambda b\rho} \tag{8}$$

where λ is an adjustable parameter. From Eqs. (2) and (8), $G(b\rho)$ can be written as

$$G(b\rho)^{-1}=(1-\lambda b\rho)=\alpha\rho\left[\frac{p}{\rho kT}-1+\frac{(\alpha-B_2)\rho}{1+0.22\lambda b\rho}\right]. \tag{9}$$

Also, the equation of state for mixtures is presented as follows [18]:

$$\frac{p}{\rho kT}=1+\rho\sum\nolimits_{ij}x_ix_j\left((B_2)_{ij}-\alpha_{ij}F_{ij}\right)+\rho\sum_{ij}x_ix_j\alpha_{ij}G_{ij}. \tag{10}$$

The summations run over all components of mixture. The interaction quantities (B_{ij} and α_{ij}) are well defined in terms of the ij intermolecular potentials, and are obtained in the same way as the corresponding quantities for single substances, either from the potential itself or from experimental data on the second Virial coefficient that G_{ij} and F_{ij} are defined in literature [18].

3. Parameters Estimation for Equation of State

3.1. Estimation by melting point for crystalline polymers

ISM equation of state requires the usage of the second Virial coefficient, B_2, along with the parameters α and b. For polymeric melts, neither the intermolecular potential nor the experimental values of B_2 are available. In this case, there are several correlation schemes usually based on the corresponding-state principle that leads to the calculation of the second Virial coefficient [19–24].

In this research, the corresponding states correlation that was previously used for pure polymer melts [8,9] was extended in order to make ISM EOS applicable to polymer blends. The resulting correlation for the second Virial coefficient reads as follows:

$$\begin{aligned}B_2\rho_\mathrm{m}=&\ 1.033-3.0069\left(\frac{T_\mathrm{m}}{T}\right)-10.588\left(\frac{T_\mathrm{m}}{T}\right)^2\\&+13.096\left(\frac{T_\mathrm{m}}{T}\right)^3-9.8968\left(\frac{T_\mathrm{m}}{T}\right)^4\end{aligned} \tag{11}$$

where ρ_m and T_m are the density and temperature both at the melting point.

It should be mentioned that melting is a transition that occurs in crystalline polymers. Melting happens when the polymer chains fall out of their crystal structures, and become a disordered liquid. In this paper, α and b were correlated by using the following pair of equations:

$$\alpha\rho_\mathrm{m}=a_1\mathrm{e}^{-c_1\left(\frac{T}{T_\mathrm{m}}\right)}+a_2\left[1-\mathrm{e}^{-c_2/\left(\frac{T}{T_\mathrm{m}}\right)^{1/4}}\right] \tag{12}$$

$$\begin{aligned}b\rho_\mathrm{m}=&\ a_1\left[1-c_1\left(\frac{T}{T_\mathrm{m}}\right)\right]\mathrm{e}^{-c_1\left(\frac{T}{T_\mathrm{m}}\right)}\\&+a_2\left\{1-\left[1+\frac{c_2}{4\left(\frac{T}{T_\mathrm{m}}\right)^{1/4}}\right]\mathrm{e}^{\frac{-c_2}{\left(\frac{T}{T_\mathrm{m}}\right)^{1/4}}}\right\}\end{aligned} \tag{13}$$

where

$$\begin{array}{ll}a_1=-0.0650, & c_1=0.6536\\ a_2=2.8542, & c_2=1.2856\end{array}.$$

The present method for calculation of the second Virial coefficient and the other two temperature-dependent parameters can be extended to mixtures using simple arithmetic mean of melting point temperature and geometric mean of liquid density at the melting point, *i.e.*,

$$(T_\mathrm{m})_{ij}=\left[(T_\mathrm{m})_i(T_\mathrm{m})_j\right]^{\frac{1}{2}} \tag{14}$$

$$(\rho_\mathrm{m})_{ij}{}^{-1/3}=1/2\left[(\rho_\mathrm{m})_i{}^{-\frac{1}{3}}+(\rho_\mathrm{m})_j{}^{-\frac{1}{3}}\right]. \tag{15}$$

The adjustable parameter of λ can be obtained from pVT data at a high density. This method for determining λ makes the whole procedure self-correcting.

3.2. Estimation by glass point for amorphous polymers

It should be mentioned that the glass transition temperature (T_g) which describes the temperature at which amorphous polymers undergo a second-order phase transition, *i.e.*, a polymer goes from a hard and glass-like state to a rubber-like state is an important property of polymers. It can be obtained by differential scanning calorimetry (DSC) method.

In this respect, the following correlation equation for B_2 using new scaling parameters, such as the surface tension γ_g and the molar density ρ_g both at the glass transition point has been