

Group estimation method for parameters of Flory–Orwoll–Vrij equation and free volume effects in polymer–solvent interaction parameters



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ABSTRACT

The Flory–Orwoll–Vrij (FOV) equation is commonly used to analyze the interaction parameters of vapors in polymer melts. The theory considers the free volume effects and requires several pure component parameters, which can be determined from the pressure–volume–temperature (PVT) data of liquids. For polymers the specific volume can be predicted using three characteristic parameters over a temperature and pressure range. For low molecular weight liquids, molar core volume, V^* , external degree of freedom, C , and interaction energy parameter, E_T , which was introduced in this study, showed linear relationships with the carbon number for several series of homologues. A group calculation method to estimate characteristic parameters was proposed in this study. The free volume effect depended on the reduced volumes of solutes and polymers. It increased when the system temperature increased. Inverse gas chromatography (IGC) data of Flory–Huggins parameters, χ , of several polar solvents in poly(vinyl chloride) and poly(tetramethylene glycol) were positive, but the exchange energy parameters, X_{12} , were negative and consistent with the molecular interaction consideration.

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1. Introduction

The knowledge of the interaction parameters between volatile organic solvent liquids and polymers is very important in the study of their miscibility [1]. Many techniques have been developed to measure these parameters [2]. Vapor sorption and inverse gas chromatography (IGC) are common techniques to measure the Flory–Huggins interaction parameters of solute vapors in high molecular weight polymers [2].

When the Flory–Huggins interaction parameter, χ , is less than 0.5, the liquid is generally characterized as a solvent for the polymer, while a value higher than 0.5 is a poor solvent and may lead to phase separation [1]. In the absence of specific interaction between a solvent and a polymer the interaction parameter is generally positive. When there is a specific interaction between a solvent and a polymer the interaction parameter can have a negative value. The solvent would be a good solvent for the polymer. Guillet et al. [3,4] demonstrated the use of the IGC method in the determination of χ . The results of χ for hydrocarbon solvents in ethylene-propylene rubber, cis-polyisoprene, and amorphous polypropylene were

around 0.4. This was near the miscibility threshold. Given the similarity in structural units between solvents and polymers these interaction parameters were higher than what is implied in the Flory–Huggins theory. This suggested that there was a mechanism increasing the χ of solvent–polymer system to a more positive value. This could be accounted for by the free volume effect as discussed later.

2. Flory–Orwoll–Vrij equation of state

For a solvent–polymer system it is known that a lower critical solution temperature can happen even when both have similar chemical structures, and can be explained by the free volume effect [5]. In the original Flory–Huggins approach of polymer solutions [1] there is no consideration of free volume effect. Later Flory et al. [6–8] used a statistical mechanical method to develop an equation of state approach that could be applied to pure materials and their mixtures. Their method is called the Flory–Orwoll–Vrij (FOV) model in this study. The equation of state of this model is:

$$\tilde{P}\tilde{V}/\tilde{T} = \tilde{V}^{1/3} / (\tilde{V}^{1/3} - 1) - 1 / (\tilde{V}\tilde{T}) \quad (1)$$

Three reduced variables are defined as:

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$$\tilde{P} = P/P^* \quad (2)$$

$$\tilde{V} = v/v^* \quad (3)$$

$$\tilde{T} = T/T^* \quad (4)$$

The value of P^* is usually very large compared with the atmospheric pressure, and the left-hand-side of Eq. (1) is small and can be ignored [6–8]. The characteristic pressure P^* , net volume or core volume per segment v^* , and characteristic temperature T^* are related to the bulk properties of polymers or solvents by the following relationships [6–8]:

$$\tilde{V}^{1/3} = 1 + \alpha T/3(1 + \alpha T) \quad (5)$$

$$P^* = \gamma T \tilde{V}^2 = \alpha T \tilde{V}^2 / \beta \quad (6)$$

where α is the thermal expansion coefficient ($\partial \ln V/\partial T$), β is the isothermal compressibility ($-\partial \ln V/\partial P$)_T, and γ is the thermal pressure coefficient ($\partial P/\partial T$)_v of liquids. Using density at one temperature and two of the three parameters α , β , and γ , the three characteristic parameters, P^* , v^* , and T^* , of Eqs. (2)–(4) can be determined. They were considered to be constants within a temperature range. These properties can be determined from the material properties of a pure substance without involvement of mixture properties. Among them v^* and T^* can be obtained more accurately using density and thermal expansion data, while P^* requires the isothermal compressibility data, which is less readily available. In the study of Flory et al. [6–8] it was shown that the P^* , v^* , and T^* for the *n*-alkane family reached constant values as the carbon number of molecule increases.

The expressions of solution thermodynamic properties of mixtures were derived in the original consideration of FOV theory [6–8]. In IGC condition the volume fraction of the polymer stationary phase can be considered as unity and volume fraction of solvent vapor to be zero. The equation simplified considerable. Eichinger and Flory [9] showed the expression of interaction parameter of a solvent at infinitesimal dilution in a polymer, χ^* , to be:

$$\chi^* = V_1^* X_{12} / (RT \tilde{V}_2) + (P_1^* V_1^* / RT) \kappa \quad (7)$$

Where

$$\kappa = 1/\tilde{V}_1 - 1/\tilde{V}_2 + 3\tilde{T}_1 \ln \left(\frac{\tilde{V}_1^{1/3} - 1}{\tilde{V}_2^{1/3} - 1} \right)$$

Here χ^* is the solvent–polymer interaction parameter calculated using the molar core volume of the solvent, V_1^* , and specific core volume of the polymer, v_2^* , in the Flory–Huggins equation. The value of χ^* is higher than χ by a quantity $\ln(\tilde{V}_1/\tilde{V}_2)$, which is a positive number for a low molecular weight solvent (component 1) dissolved in a polymer melt (component 2). The first term in the right-hand-side of Eq. (7) is the interaction term and the second term is the free volume. The dimensionless κ depends the free volumes of both solutes and polymers. From the interaction parameter χ^* the exchange energy parameter X_{12} can be calculated. The advantage of using this method in the analysis of the solvent–polymer interaction of vapor sorption at infinitesimal dilution or IGC data is that only properties of pure components are

needed, and no other adjustable parameter is used beyond those already used in the Flory–Huggins method. Huang and Madey [10] applied this method to gas chromatographic data of several low molecular weight stationary phases between 50 and 80 °C and found that the free volume term contributed a positive value of 20–50 cal/mole to the free energy of solution. This corresponds to 0.03–0.1 in the value of χ . This number would be higher in the sorption of solvent vapor in a polymer and particularly at higher temperature. The purpose of this study is to extend the previous study to polymeric stationary phases at higher temperatures, and to propose a group addition method for estimating the characteristic parameters of the FOV model.

3. Characteristic volume of polymers

Pressure–volume–temperature (PVT) data of polymers were available from a compilation by Zoller and Walsh [11]. The characteristic parameters were calculated using data between 50 and 100 °C above the glass transition temperature. Fig. 1 showed the comparison between data of polystyrene and predictions based on the FOV equation and three characteristic parameters. The similar comparison for polycarbonate was shown in Fig. 2. The specific volume was predicted reasonably well for both polymers at atmospheric pressure and 20 MPa (≈ 200 atm). The predicted specific volume was higher than literature data at 40 MPa. This suggested a limitation of the FOV equation at higher pressures. The use of the FOV equation may be limited to pressure ranges below 20 MPa, which is the range in which many of the phase equilibrium studies were made.

4. Characteristic parameters of organic liquids

A collection of density, thermal expansion coefficient, and isothermal compressibility data of low molecular weight organic liquids was made by Allen et al. [12]. The parameters of selected chemicals are shown in Table 2. The data were used to estimate the characteristic parameters. It was found that when v^* was multiplied by the molecular weight of solvents to obtain the molar core volume, V^* , there was a linear relationship with the carbon number for each homologous series. This was shown in Fig. 3 and linear lines were observed. The lines had similar slopes, which indicated that for each increment of one methylene segment, the increase of core volume was a constant regardless of the functional group attached at the end. This opened the possibility of calculating core volume by a group addition method. In contrast, T^* and P^* of homologous

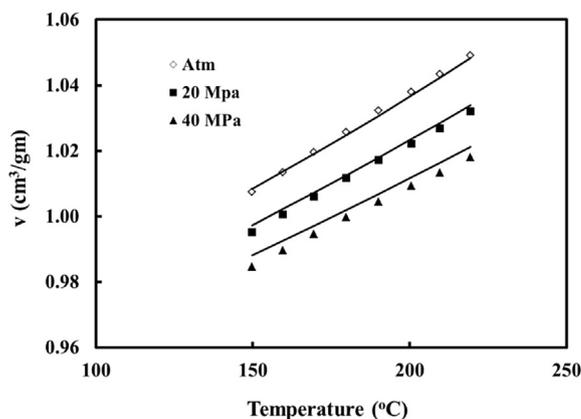


Fig. 1. Prediction of density of polystyrene using Flory–Orwoll–Vrij equation at atmosphere pressure, 20 MPa, and 40 MPa with the following parameters: $v^* = 0.84 \text{ cm}^3/\text{gm}$, $P^* = 135 \text{ cal}/\text{cm}^3$, and $T^* = 8600 \text{ K}$.

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