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Thermodynamics of blends of PEO with PVAc: application of the Sanchez–Lacombe lattice-fluid theory

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Abstract

Sanchez–Lacombe (SL) lattice-fluid theory was used to predict the miscibility of the PEO/PVAc blending system. Integral interaction parameters, *g* of this polymer pair were calculated by using SL theory. And the effect of the temperature, composition of blends and molecular weight of PVAc on the extent of their miscibility has been discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Thermodynamics; Blends; Interaction parameter

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1. Introduction

The first description of statistical thermodynamics of polymer solutions was proposed by Flory [1] and Huggins [2]. It is a rigid lattice model that ignores free volume. Since then, various theories have been presented that allow for the possibility of volume changes. Prigogine et al. [3,4] presented a cell model theory which introduced a free volume by assuming a hard-sphere repulsive potential for the segments of the polymer chain moving in a square-well potential. Flory et al. [5,6] presented a modified version of this theory. The main difference was the replacement of the generalized Lennard-Jones potential by a van der Waals type potential. On the other hand, another quantitative theory taking the compressibility of both components into account has been developed by Sanchez and Lacombe [7–9]. It is similar to the Flory–Huggins theory, but a free-volume term is introduced via vacant lattice sites. Based on this lattice-fluid model Panayioton [10] presented a modified molecular theory of *r*-mer fluid mixtures which took into account the differences of molecular shape.

In recent years, the study of the miscibility and phase behavior of polymer blends has attracted a large amount of theoretical and experimental interest. One of the polymer pairs is poly(ethylene oxide) (PEO) and poly(vinyl acetate) (PVAc). They are known to be compatible by both theoretical prediction and experimental results [11–21]. Kalfoglou et al. [11,12], Munoz et al. [13], Martuscelli et al. [14–16] and our previous work [17] had discussed the miscibility of this blend system from many aspects including morphology, dynamic mechanical properties, rheological properties, thermal behavior, crystallization and viscosity in dilute solution. But these results do not allow us to draw quantitative conclusions on miscibility of PEO with PVAc. In our previous communication [18,19], interaction parameters of PEO–PVAc blends with different compositions and temperatures were calculated based on Flory solution theory modified by Hamada et al. [20]. Results showed that interaction parameters of PEO–PVAc blends were negative and increased with enhancing the content of PEO and the temperature. Further, cloud points and heats of mixing of this polymer pair were detected by using DSC on the assumption that values of heats of mixing were considered to be heats of demixing with opposite sign [21–23].

In this paper, the scaling parameters of PEO and PVAc obtained by means of fitting pressure–volume–temperature (PVT) data which were measured with PVT dilatometry were reported. The spinodal and binodal curves of blends of PEO and PVAc with different molecular weights were calculated by using Sanchez–Lacombe (SL) lattice-fluid theory. And the dependence of interaction parameters, which were used to characterize their miscibility and miscible extent upon the temperature and the composition of this polymer pair, were tentatively studied.

2. Theoretical background

In the lattice-fluid theory, as formulated by Sanchez and

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Lacombe [7–9], the Gibbs energy of mixing for polymer–polymer blends is related to the Gibbs energy per mer (indicated by the double bar) of the mixture (index M) and that of the pure components (subscripts 1 or 2) by:

$$\Delta G_{\mathrm{M}} = rN[\overline{\overline{G}}_{\mathrm{M}} - (\phi_1\overline{\overline{G}}_1 + \phi_2\overline{\overline{G}}_2)] \tag{1}$$

where rN is the total number of lattice sites occupied in the mixture and $rN = r_1^0N_1 + r_2^0N_2 = r_1N_1 + r_2N_2$.

The thermal equation of state and Gibbs energy per mer of pure component reads:

$$\tilde{\rho}_i^2 + \tilde{P}_i + \tilde{T}_i\left[\ln(1-\tilde{\rho}_i) + \left(1 - \frac{1}{r_i^0}\right)\tilde{\rho}_i\right] = 0 \tag{2}$$

$$\overline{\overline{G}}_i = \epsilon_{ii}^*\left\{-\tilde{\rho}_i + \tilde{P}_i\tilde{v}_i + \tilde{T}_i\left[(\tilde{v}_i - 1)\ln(1-\tilde{\rho}_i) + \frac{1}{r_i^0}\ln\left(\frac{\tilde{\rho}_i}{\omega_i^0}\right)\right]\right\}_{i=1\text{ or }2} \tag{3}$$

and those of the mixture:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1-\tilde{\rho}) + \left(1 - \frac{1}{r}\right)\tilde{\rho}\right] = 0 \tag{4}$$

$$\overline{\overline{G}}_{\mathrm{M}} = \epsilon^*\left\{-\tilde{\rho} + \tilde{P}\tilde{v} + \tilde{T}\left[(\tilde{v} - 1)\ln(1-\tilde{\rho}) + \frac{1}{r}\ln\tilde{\rho} + \frac{\phi_1}{r_1}\ln\frac{\phi_1}{\omega_1} + \frac{\phi_2}{r_2}\ln\frac{\phi_2}{\omega_2}\right]\right\} \tag{5}$$

where ϕ_i is the close-packed volume fraction of component i. $\tilde{\rho}_i$, $\tilde{P}_i$, $\tilde{v}_i$, $\tilde{T}_i$ and $\tilde{\rho}$, $\tilde{P}$, $\tilde{v}$, $\tilde{T}$ are the reduced parameters of density, pressure, volume and temperature of the pure components and those of the mixtures, respectively. They are defined by their actual pressure (P), volume (V) and temperature (T) and scaling parameters (denoted with asterisks) as follows:

$$\tilde{P}_i = P/P_i^* \qquad \tilde{P} = P/P^* \tag{6}$$

$$\tilde{T}_i = T/T_i^* \qquad \tilde{T} = T/T^* \tag{7}$$

$$\tilde{v}_i = V_i/V_i^* \qquad \tilde{v} = V/V^* \tag{8}$$

$$\tilde{\rho}_i = 1/\tilde{v}_i \qquad \tilde{\rho} = 1/\tilde{v} \tag{9}$$

$$V_i^* = r_i^0N_iv_i^* \qquad V^* = (r_1N_1 + r_2N_2)v^* \tag{10}$$

Scaling parameters can also be expressed in terms of the interaction energies ϵ_{ii}^* for pure component and ϵ^* for mixtures.

$$P_i^* = \epsilon_{ii}^*/v_i^* \qquad P^* = \epsilon^*/v^* \tag{11}$$

$$T_i^* = \epsilon_{ii}^*/\mathrm{k} \qquad T^* = \epsilon^*/\mathrm{k} \tag{12}$$

where P_i^*, T_i^*, v_i^* and P^*, T^*, v^* are obtained by fitting the equation of state to PVT data for pure components.

The closed-packed volume of a mer, v^*, and the average number of mers for a molecule, r, in the mixture are expressed as:

$$1/v^* = \phi_1/v_1^* + \phi_2/v_2^* \tag{13}$$

$$1/r = \phi_1/r_1 + \phi_2/r_2 \tag{14}$$

r_i^0 and r_i are the number of lattice sites occupied by a molecule of component i in the pure fluid and in the fluid mixture, respectively. For the pure component r_i^0 can be calculated from the following relationship:

$$r_i^0 = M_iP_i^*/\mathrm{k}T_i^*\rho_i^* \tag{15}$$

where M_i is the molecular weight of component i, ρ_i^*, the close-packed density of component i, and k the Boltzmann constant.

In the close-packed state, ω_i and ω_i^0 are number of configurations available to a r_i-mer and r_i^0-mer [7,24] and

$$\omega_i = \delta_ir_i/\sigma_i\ \mathrm{e}^{r_i-1} \tag{16}$$

$$\omega_i^0 = \delta_i^0r_i^0/\sigma_i^0\ \mathrm{e}^{r_i^0-1} \tag{17}$$

where δ_i, δ_i^0 and σ_i, σ_i^0 are the flexibility parameters and the symmetry numbers of an r_i-mer and of an r_i^0-mer, respectively. In the present case, $\sigma_i = \sigma_i^0 = 1$ and

$$\delta_i = z(z-1)^{r_i-2} \tag{18}$$

$$\delta_i^0 = z(z-1)^{r_i^0-2} \tag{19}$$

where z is the coordination number of the lattice ($z = 12$).

In a binary mixture there are three possible contacts with the non-zero interaction energy: 1–1, 2–2 and 1–2. Therefore ϵ^* consists of the three interaction energies according to the following relation:

$$\epsilon^* = \phi_1^2\epsilon_{11}^* + 2\phi_1\phi_2\epsilon_{12}^* + \phi_2^2\epsilon_{22}^* \tag{20}$$

where ϵ_{12}^* is the interaction energy of a mer of component 1 (or 2) when it is surrounded by z-mers component 2 (or 1).

Integral Flory–Huggins interaction parameter, g, is defined in terms of the residual free energy of mixing per mer ($\Delta\overline{\overline{G}}^{\mathrm{R}}$) as follows [25]:

$$\frac{\Delta\overline{\overline{G}}^{\mathrm{R}}}{\mathrm{k}T} = \phi_1\phi_2g \tag{21}$$

where

$$\Delta\overline{\overline{G}}^{\mathrm{R}} = \Delta\overline{\overline{G}}_{\mathrm{M}} - \Delta\overline{\overline{G}}_{\mathrm{M}}^{\mathrm{comb}} \tag{22}$$

Table 1
Molecular characteristics of PEO and PVAc

Polymer	Source	M_w	M_n	M_w/M_n
PEO46	Fluka	46 200	40 000	1.15
PEO100	Fluka	126 000	33 000	3.82
PVAc17	Aldrich	16 800	8900	1.89
PVAc50	Aldrich	49 500	38 100	1.30
PVAc126	Aldrich	126 000	84 700	1.50

$\Delta\overline{\overline{G}}_M^{\mathrm{comb}}$, the combinatorial Gibbs energy is given as:

$$\Delta\overline{\overline{G}}_M^{\mathrm{Comb}} = \mathrm{k}T\left(\frac{\phi_1}{r_1}\ln\frac{\phi_1}{\omega_1} + \frac{\phi_2}{r_2}\ln\frac{\phi_2}{\omega_2}\right) - \mathrm{k}T\left(\frac{\phi_1}{r_1^0}\ln\frac{1}{\omega_1^0} + \frac{\phi_2}{r_2^0}\ln\frac{1}{\omega_2^0}\right) \tag{23}$$

Eqs. (3), (5) and (20)–(23) yield

$$g = \frac{1}{\mathrm{k}T\phi_1\phi_2}\Bigg\{[\epsilon^*(-\tilde{\rho} + \tilde{P}\tilde{v}) - \phi_1\epsilon_{11}^*(-\tilde{\rho}_1 + \tilde{P}_1\tilde{v}_1) - \phi_2\epsilon_{22}^*(-\tilde{\rho}_2 + \tilde{P}_2\tilde{v}_2)] + \mathrm{k}T\Bigg\{\Bigg[(\tilde{v} - 1)\ln(1 - \tilde{\rho}) + \frac{1}{r}\ln\tilde{\rho}\Bigg] - \phi_1\Bigg[(\tilde{v}_1 - 1)\ln(1 - \tilde{\rho}_1) + \frac{1}{r_1^0}\ln\tilde{\rho}_1\Bigg] - \phi_2\Bigg[(\tilde{v}_2 - 1)\ln(1 - \tilde{\rho}_2) + \frac{1}{r_2^0}\ln\tilde{\rho}_2\Bigg]\Bigg\}\Bigg\} \tag{24}$$

which reduces for large values of r and r_i^0 to

$$g = \frac{1}{\mathrm{k}T\phi_1\phi_2}\{[\epsilon^*(-\tilde{\rho} + \tilde{P}\tilde{v}) - \phi_1\epsilon_{11}^*(-\tilde{\rho}_1 + \tilde{P}_1\tilde{v}_1) - \phi_2\epsilon_{22}^*(-\tilde{\rho}_2 + \tilde{P}_2\tilde{v}_2)] + \mathrm{k}T[(\tilde{v} - 1)\ln(1 - \tilde{\rho}) - \phi_1(\tilde{v}_1 - 1)\ln(1 - \tilde{\rho}_1) - \phi_2(\tilde{v}_2 - 1)\ln(1 - \tilde{\rho}_2)]\} \tag{25}$$

3. Experimental section

3.1. Materials

The source and molecular characteristics of PEO and PVAc in this work are reported in Table 1. PEO samples were used as received. PVAc was fractionated by using a step precipitation method. Acetone and petroleum ether were used as solvent and precipitating agent, respectively. The molecular weight of PEO and PVAc fractions were characterized by the GPC method.

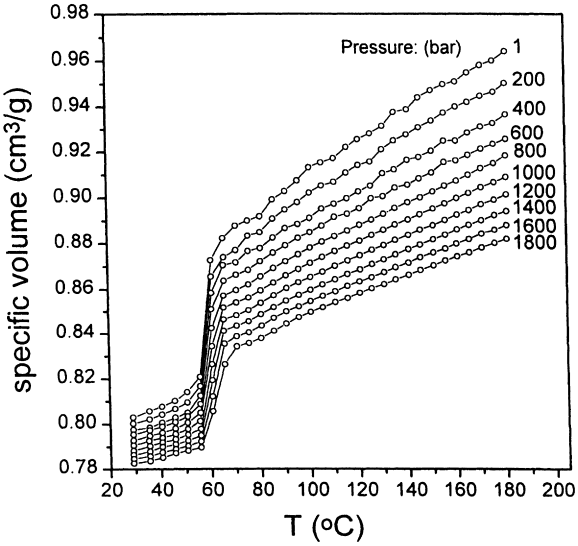

Fig. 1. Specific volume of PEO100 as a function of temperature and pressure.

3.2. Measurement of cloud points

Cloud points of PEO/PVAc blends were determined by using a Perkin–Elmer DSC7 scanning calorimeter. A series of onset temperatures of endothermic peaks measured in the range of phase separation temperature with different heating rates were obtained. The onset temperature extrapolated to zero heating rate was taken as the "cloud points" of blends. A detailed description of this experimental method, measuring procedure and sample preparation were reported in our previous paper [19].

3.3. Measurement of P,V,T parameters

The *P,V,T* parameters of PEO and PVAc were measured with a high-pressure dilatometer, pvT100 (SWO Polymertechnik GmbH) with an isothermal cooling procedure at a rate of 5°C/min. The measurement ranges for temperature and pressure are 30–180°C and 200–1800 bar, respectively. Each step difference for temperature and pressure measurements is 5°C and 200 bar. Specific volumes of PEO and PVAc under 1 bar pressure which implies atmospheric pressure are estimated from the high-pressure data based on Tait equation-of-state [26].

4. Results and discussion

The PVT data of PEO100 and PVAc126 are shown in Figs. 1 and 2, respectively. In these two figures, open circles represent the experimental specific volume as a function of temperature and pressure. The data at 1 bar were obtained by using extrapolating method with the data at high pressure and the Tait equation of state. The scaling parameters of these two polymers are calculated by fitting the equation of state, i.e. Eq. (2), with the selected experimental PVT

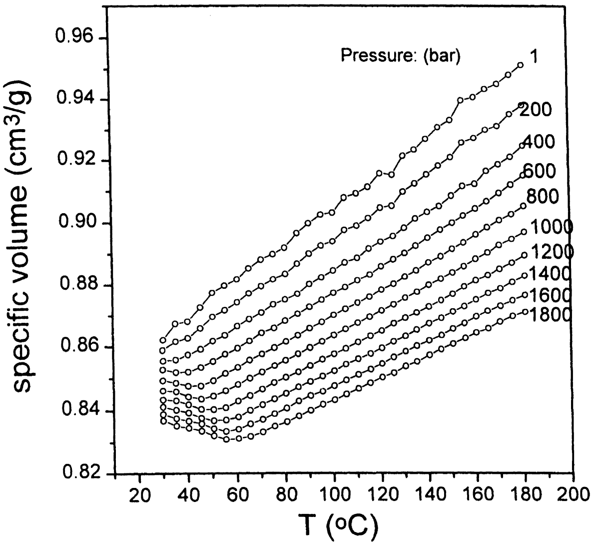

Fig. 2. Specific volume of PVAc126 as a function of temperature and pressure.

data. Since phase separation occurs above the melting temperature of PEO, the selected PVT data of two polymers are in the range of temperature 75–160°C and pressure 0–1800 bar. The calculated scaling parameters are listed in Table 2.

By using Eqs. (1), (3) and (5) etc. provided in Section 2 and scaling parameters of these two polymers, phase diagrams of this blending system are calculated and shown in Fig. 3. A new method [27,28] which allows us to calculate the spinodal and binodal curves on the basis of the Gibbs energy of mixing ΔG is adopted. In this calculation, no derivatives of ΔG with respect to the composition variables are required. The calculation procedure of the spinodal line in binary systems is demonstrated below where ΔG is written as a function of the volume fraction. The volume fraction is divided into *n* points. For each of these points it is checked whether the system is unstable or not. If the overall value of ΔG for the demixed system ($\Delta G^{\text{o.a.}}$) is less then ΔG of the homogeneous system the overall composition lies within the unstable area, because here the beginning of the demixing process leads to a decrease in ΔG (no energy barrier). Otherwise the overall composition lies in the stable or the metastable range. Checking all points yields the entire unstable area, and thus the spinodal line as its boundary. For the overall composition, a set of volume fractions is found for which $\Delta G^{\text{o.a.}}$ has its minimum value. Connecting these volume fractions yields the binodal line.

Table 2
Scaling parameters of PEO and PVAc

	P^* (atm)	ρ^* (g/cm^3)	T^* (K)
PEO	6803.8	1.260	584.3
PVAc	5179.1	1.243	623.0

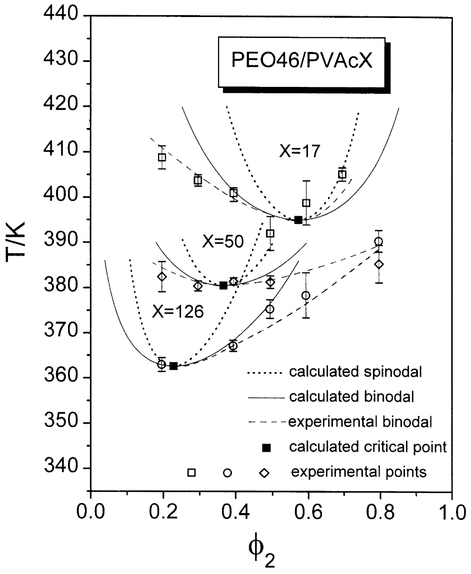

Fig. 3. Phase diagrams of PEO46/PVAcX($X = 17$, 50, 126) blending system, where $\epsilon^*_{12}/\text{k} = 603.855$ for PEO46/PVAc17, $\epsilon^*_{12}/\text{k} = 603.785$ for PEO46/PVAc50 and $\epsilon^*_{12}/\text{k} = 603.760$ for PEO46/PVAc126.

The phase diagrams of the blending system of PEO46 and PVAc with different molecular weight blending system are given in Fig. 3. The dotted and solid lines in Fig. 3 represent the spinodal and binodal curves calculated with the SL theory. The open points are experimental "cloud points" measured by DSC method and dash lines are experimental binodal curves. Obviously, phase diagrams with characteristics of lower critical solution temperature (LCST) are obtained for this blending system. A good agreement can be seen between experimental and calculated binodals in the range of ϕ_2 around the critical compositions. With increasing molecular weight of PVAc, the critical temperatures (T_c) and compositions (ϕ_{2c}) shift to low temperature and high PEO concentration as shown in Fig. 3.

Values of ϵ^*_{12}/k as a function of $M_2^{-1/2}$ (molecular weights of PVAc) are shown in Fig. 4. It is found that ϵ^*_{12}/k is linearly related to $M_2^{-1/2}$. In a binary polymer blending system, de Gennes [29] has proposed a scaling relationship about the dependence of the Flory–Huggins interaction parameter upon the molecular weights of blending components:

$$\chi_c = \frac{1}{2}\left(\frac{1}{\sqrt{M_1}} + \frac{1}{\sqrt{M_2}}\right)^2 \tag{26}$$

where χ_c is the critical value of Flory–Huggins interaction parameter, M_1 and M_2 are the molecular weight of component 1(PEO) and 2(PVAc), respectively. In this calculation the molecular weight of PEO (M_1) is fixed, then Eq. (26) can be rewritten as follows, when the term of $1/M_2$ is ignored [30]:

$$\chi_c \propto M_2^{-1/2} \tag{27}$$

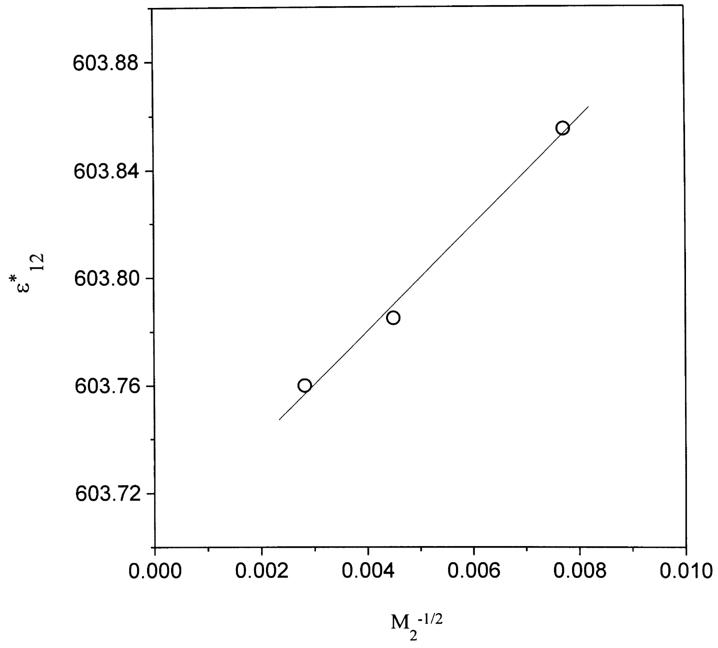

Fig. 4. $\epsilon^*_{12}/\mathrm{k}$ as a function of $M_2^{-1/2}$.

Because both χ_c in Flory–Huggins theory and ϵ^*_{12} in LF theory represent the interaction of asymmetry segments between components, we can give the similar equation for ϵ^*_{12} [30]

$$\epsilon^*_{12}/\mathrm{k} \propto M_2^{-1/2} \tag{28}$$

where k is the Boltzmann constant. Fig. 4 is consistent with this feature. These suggest that it is reasonable to predict the phase behavior of PEO/PVAc blending system with SL theory.

Integral Flory–Huggins interaction parameters, *g*, of this blending system were calculated on the basis of Eqs. (21)–(25). Values of *g* of PEO46/PVAc*X* ($X = 17$, 50 and 126) as a function of $1/T$ were shown in Fig. 5. It decreases linearly with $1/T$. This feature suggests that the miscible extent of these blends is inversely proportional to the temperature. This result is consistent with the conclusion that we obtained by using Flory solution theory modified by Hamada et al. [20]. The composition dependence of *g* was also shown in Fig. 5. With increasing the content of PVAc (ϕ_2), it decreased. This result means that the miscibility increases with increasing PVAc content of blends. A similar trend was obtained in our previous report [18]. It was also seen from this figure that *g* decreased with decreasing the molecular weight of PVAc. It suggested that the miscibility and the extent of miscibility of PEO/PVAc blends enhanced with decreasing molecular weight of PVAc.

5. Conclusion

1. Phase behavior of PEO/PVAc blending system was investigated in this work. Spinodal and binodal lines of PEO and PVAc blends were obtained by using SL lattice-fluid theory. The calculated binodal lines are nearly consistent with the experimental one, which was determined by using DSC method.
2. Integral interaction parameters, *g*, of this blending system were determined and used to characterize their miscibility and miscible extent. They decreased with increasing the content of PVAc and with decreasing the temperature and the molecular weight of PVAc. This suggested that the miscible extent of this blending system depended upon the composition, temperature and the molecular weight of blending components.

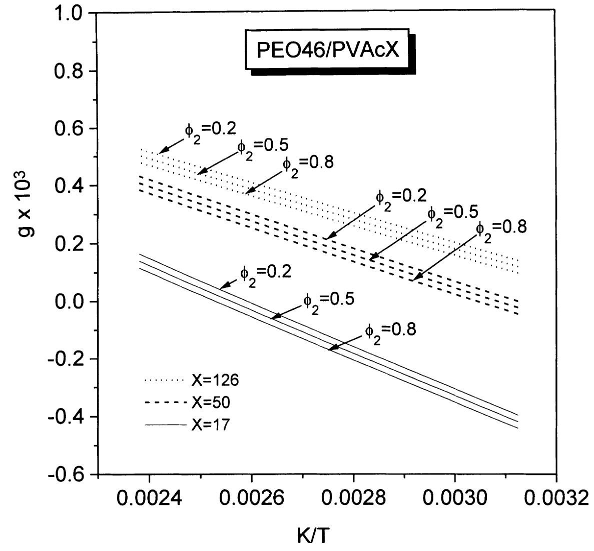

Fig. 5. Temperature dependence of interaction parameters *g* for blends of PEO46/PVAc*X*($X = 17$, 50, 126) at the different constant volume fraction of PVAc.

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