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Theoretical Consideration on the Number of External Degrees of Freedom and Its Application to Poly(Dimethylsiloxane) Solutions

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Summary

The Flory theory of polymer solution was modified by assuming the non-additivity of the number of the degree of external freedom for a binary mixture and applied the modified Flory theory to poly(dimethylsiloxane)-solvent systems. This theory can reproduce the experimental results of the interaction parameter χ and the excess volume of mixing, which the Flory theory failed to reproduce.

Introduction

Thermodynamic theories based on the concept of free volume have been used to explain various thermodynamic phenomenon of polymer solutions. Flory(1965) proposed a new theory applicable to various non-polar polymer solutions combining Tonks' hard sphere model with a van der Walls attractive energy part. The applicability of his theory was verified for polyethylene solution(Orwoll and Flory, 1967, Hamada et al. 1973) and polyisobutylene (Eichinger and Flory, 1968a,b,c) solution. For natural rubber(Eichinger,1968d), polystyrene(Flory and Höcker,1971, Höcker and Flory,1971a,b) and poly(dimethylsiloxane)(PDMS)(Flory and Shih,1972) solutions, however, the Flory theory requires an entropic correction parameter Q_{12}, the physical meaning of which is obscure. Especially for PDMS solution, his theory leads to a very large correction for the interaction parameter χ and to overestimation of the excess volume of mixing V^E. In this paper, the Flory theory was modified from theoretical consideration on the number of external degrees of freedom and the modified Flory theory was applied to PDMS-solvent systems.

Theory

According to the configurational partition function given by Flory and Prigogine's approximation to the number of external degrees of freedom(Prigogine a,b),the partition function Z for the system comprizing N r-mers can be written as

$$Z = Z_{comb}[q_{int}(T)^{Nr}(2\pi mkT/h^2)^{3Nrc/2}[g(v^{1/3} - v^{*1/3})^3]^{Nrc} \times \exp(-E_o/kT) \qquad (1)$$

where Z_{comb} is the combinatorial factor including the communal entropy, $q_{int}(T)$ is the part related to the internal degrees of freedom, g is the geometric factor, m, v, and v^* are the mass, volume and core volume per segment, respectively, 3c is the number of external degrees of freedom per segment and E_o is the mean internolecular energy given by

$$E_o = -Nrs\eta/2v \tag{2}$$

where s is the number of intermolecular contact sites per segment and $-\eta/v$ is the intermolecular energy per contact. From eq.(1), the reduced partition function is given by

$$Z = Z_{comb}[q_{int}(T)]^{Nr}[(2\pi mkT/h^2)^{1/3}]^{3Nrc} \cdot (\tilde{v}^{1/3} - 1)^{3Nrc}\exp(Nrc/\tilde{v}\tilde{T}) \tag{3}$$

and the reduced equation of state is

$$\tilde{p}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3} - 1) - 1/\tilde{v}\tilde{T} \tag{4}$$

where $\tilde{p}$, $\tilde{v}$, and $\tilde{T}$ are the reduced variables of pressure, volume and temperature, respectively and are defined by

$$\tilde{p} = p/p^* \tag{5}$$

$$\tilde{v} = v/v^* \tag{6}$$

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

where p^*, v^*, and T^* are the characteristic parameters.

The characteristic parameter of pressure p for a binary mixture is defined by

$$p^* = \phi_1 p_1^* + \phi_2 p_2^* - \phi_1\theta_2 X_{12} \tag{8}$$

where ϕ_i and θ_i are the segment fraction and the site fraction, X_{12} is the exchange interaction parameter defined by

$$X_{12} = (s_1/2v^{*2})(\eta_{11} + \eta_{22} - 2\eta_{12}) \tag{9}$$

where η_{11}, η_{22}, η_{12} represent constant characterizing the energy of interaction for a pair between the respective point.

Flory assumed that the number of external degrees of freedom,c,for a binary mixture is additive with respect to concentration. But from the discussion of equation of state used by Flory (Fujisawa et al.1980),the excess thermal pressure coefficient of PDMS-benzene system(Fujisawa et al.1976), and P-V-T relation of PDMS-benzene solution based on correspondence principle by Kubota et al(1977), we conclude that disagreement between experimental and calculated values of PDMS-solvent system don't comes from the inadequacy of equation of state used by Flory,but comes from the combining rule assumed by Flory. Thus the number of external degrees of freedom for a binary mixture is assumed by

$$c = \phi_1 c_1 + \phi_2 c_2 - \phi_1 \theta_2 (v^*/k)\delta \tag{10}$$

where δ is the parameter indicating the deviation from the additivity of the number of external degrees of freedom. Lin (1970) assumed the similar equation to eq.(10). By the use of eq.(10), the characteristic parameter of temperature for a binary mixture is calculated by

$$1/T^* = (\phi_1 p_1/T_1^* + \phi_2 p_2/T_2^* - \phi_1 \theta_2 \delta)/(\phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \theta_2 X_{12}) \tag{11}$$

Accrding to Flory, by differentiation of residual free energy followed by substitution from the eq.(4), the chemical potential of component 1 is given by

$$\begin{aligned}(\mu_1 - \mu_1{}^o)^R = {} & (-3/2) p_1^* v_1^* \tilde{T}_1 \ln(m/m_1) + 3v_1^* T\delta \ln K\theta_2^2 - \\ & (3/2)(m_1 - m_2)/(\phi_1 m_1 + \phi_2 m_2)(p^* v^* \tilde{T})\phi_2 + \\ & 3p_1^* v_1^* \tilde{T}_1 \ \ln(\tilde{v}_1{}^{1/3} - 1)/(\tilde{v}^{1/3} - 1) + 3v^* T\delta \times \\ & [\ln(\tilde{v}^{1/3} - 1)]\theta_2{}^2 + p_1{}^* v_1{}^* (1/\tilde{v}_1 - 1/\tilde{v}) + (v_1^* X_{12}/\tilde{v})\theta_2^2\end{aligned} \tag{12}$$

where $K = (2\pi mkT/h^2)^{1/2}(gv^* e^3)^{1/3}$, $m = \phi_1 m_1 + \phi_2 m_2$ and we use $g = 4\sqrt{2}\pi/3 (z = 12)$.

Interaction parameter χ is defined by

$$\chi = (\mu_1 - \mu_1{}^o)^R/(RT\phi_2^2) \tag{13}$$

The enthalpy of mixing $\Delta H^M(\infty)$ to infinitive dilution can be written

$$\begin{aligned}\Delta H^M(\infty) = {} & (v^*_{sp;2}/\tilde{v}_1)\{p_2^*[(v_1/\tilde{v}_2 - 1 - (\alpha_1 T)(1 - T_1^*/T_2^*)] + (s_2/s_1)\times \\ & [(1 + \alpha_1 T)X_{12} - (\alpha_1 T/2)(9 + 8\alpha_1 T/3 + 4\alpha_1 T)(T_1^*\delta)]\}\end{aligned} \tag{14}$$

where $v^*_{sp;2}$ is specific characteristic volume of component 2, s_2/s_1 is the ratio of the surface area per segment for polymer to that for solvent and α_1 the thermal expansion coefficient of component 1. The ratio of the excess volume V^E to the sum V^o of the volumes of the pure components is given by

$$V^E/V^0 = \tilde{v}/\tilde{v}^o - 1 \tag{15}$$

where $\tilde{v}^o = \phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2$

Results and Discussion

In Figure 1 and 2,, the interaction parameter χ is plotted against the segment fraction for PDMS-benzene and PDMS-cyclohexane. The full line are calculated by the use of eq.(12). The exchange interaction parameter X_{12}, the parameter δ and s_2/s_1 used in calculation are shown in Table I. These values are chosen to reproduce the experimental results best. For comparison,

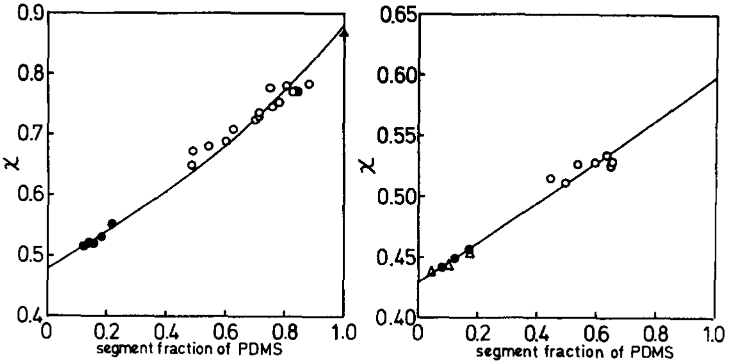

Figure 1 (left) and 2(right). Interaction parameter χ plotted against segment fraction for PDMS-benzene(Fig.1) and PDMS-cyclohexane(Fig.2).

Table I. X_{12},δ, and s_2/s_1 values used in this work and X_{12},Q_{12}, and s_2/s_1 values used in calculation by Flory theory.

	This Work			Flory Theory		
Solvent	X_{12}	δ	s_2/s_1	X_{12}	Q_{12}	s_2/s_1
benzene[a]	24	0.0078	0.76	22	-0.042	0.758
cyclohexane[a]	13	0.0057	0.92	8	-0.039	0.83
chlorobenzene[a]	16	0.0056	0.73	11	-0.064	0.714
MEK[b]	34	0.0068	0.76	24.6	-0.0596	0.69
EBK[b]	18	0.0043	0.80	14.5	-0.0322	0.70

Table II. Calculated and observed excess volume ratios and heat of infinite dilution

	Experimental(at 25°C)		Calculated(at 25°C)	
Solvent	V^E/V_o	$\Delta H^M(\infty)$	V^E/V_o	$\Delta H^M(\infty)$
benzene	$-0.06\mathrm{x}10^{-2,a}$	11 J/g[c]	$0.34\mathrm{x}10^{-2}$	7 J/g
cyclohexane	$+0.06\mathrm{x}10^{-2,a}$	5.2 J/g[c]	$0.14\mathrm{x}10^{-2}$	3 J/g
chlorobenzene	$-0.50\mathrm{x}10^{-2,a}$	7.53J/cm^3 [c]	$0.18\mathrm{x}10^{-2}$	6 J/g
MEK	$-0.030\mathrm{x}10^{-2,b}$	14.3J/g[b]	$0.69\mathrm{x}10^{-2}$	14.3J/g
EBK	$-0.116\mathrm{x}10^{-2,b}$	8.8 J/g[b]	$0.17\mathrm{x}10^{-2}$	8.8J/g

a) Flory and Shih, 1972.
b) Shiomi et al. 1980.
c) Delmas et al. 1964

X_{12} and Q_{12} values calculated by the original Flory theory are also listed. The reduced and reduction parameters(v, T, v_{sp}*, T^*, and p*) for components were determined from the specific volume v_{sp}, the thermal expansivity α, and the thermal pressure coefficient γ according to Flory's method(Flory 1965). The core volume of polymer per segment, v_2* was assumed to be that of the solvent. (this assumption means $r_1 = 1$ in the Flory theory). As shown in Figure 1 and 2, good agreement between experimental values and calculated values using eq.(12) without Q_{12} parameter. Also for systems, PDMS-chlorobenzene, PDMS-methyl ethyl ketone (MEK), PDMS-ethyl n-butyl ketone(EBK), good results were obtained. In Table II, the calculated and observed excess volume ratio V^E/V^o and heat of infinite dilution $\Delta H^M(\infty)$ are shown. Values of V^E/V^o obtained by the Flory theory are 0.80x10^{-2}, 0.71x10^{-2}, 0.25x10^{-2}, i.ix10^{-2} and 0.47x10^{-2} for PDMS-benzene, cyclohexane, chlorobenzene, MEK, and EBK, respectively. Agreements of V^E/V^o calculated by the modified Flory theory with experimental values are better than those by the Flory theory. Kubota et al(1977) measured the PVT relation for PDMS-solvent systems and examined the combining rules without using any model except the assumption of the corresponding state principle. According to their results, the number of external degrees of freedom for the mixtures varies in a nonlinear fashion with respect to concentration and is smaller than that obtained by the linear combination of the values for both pure components. This is a strong evidence of our assumption of non-additivity of the number of external degrees of freedom for a binary mixtures.

We conclude that the Flory theory is improved by assuming non-additivity of the number of external degrees of freedom. Further investigation will be published elsewhere(Shiomi et al. 1980, Hamada,1980).

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