Thermodynamics of oligomer blends of poly(methylphenylsiloxane) and polystyrene

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Heats of mixing to infinite dilution $\Delta H^M(\infty)$, excess volumes V^E and cloud-point curves were experimentally determined for an upper critical solution temperature type of system, the poly(methylphenylsiloxane)/polystyrene oligomer blend. $\Delta H^M(\infty)$ was positive and V^E negative. Flory's equation-of-state theory with modified combining rules was applied to this system. The theory with the positive value of the exchange enthalpy parameter reproduced the experimental thermodynamic properties except for the location of the maximum point in the cloud-point curves.

(Keywords: thermodynamics; equation-of-state theory; oligomer blends; poly(methylphenylsiloxane); polystyrene)

INTRODUCTION

Usually polymer blends consisting of high-molecular-weight polymers are lower critical solution temperature (*LCST*) types, while low-molecular-weight polymer blends are upper critical solution temperature (*UCST*) types[1–3]. (Recently, in some high-molecular-weight copolymer blends a *UCST* has been found[4,5].) In the early investigations of polymer blends, Allen *et al.*[6] reported that the oligomer blend of poly(isobutylene)/poly(dimethylsiloxane) had a *UCST* and that its heats of mixing were endothermic. Since that report, some blends containing oligomers have been found to be *UCST* type[7].

According to the equation-of-state theory[8–11], for *LCST*-type systems the exchange enthalpy parameter is expected to be negative, which means that a specific interaction may be dominant in the system. For *UCST*-type systems, on the other hand, the exchange enthalpy parameter may be positive. In the case of oligomer blends, two constituent polymers can be miscible with each other due to the contribution of the combinatorial entropy caused by low molecular weights, and also there may exist an *LCST* as well, at least theoretically. In previous papers[12,13], we presented thermodynamic properties for the *LCST*-type polymer blend, poly(vinyl methyl ether)/polystyrene, and applied the modified equation-of-state theory[14–16] to this system. Consequently, the enthalpy of mixing and excess volume were negative, and the various thermodynamic properties could be reproduced well by the theory with a negative value of the exchange enthalpy parameter.

In this paper, we will describe the thermodynamics, especially the application of the equation-of-state theory, for a *UCST*-type system, the oligomer blend of poly(methylphenylsiloxane)/polystyrene, which is expected to have positive heats of mixing and a positive exchange enthalpy.

THEORETICAL BACKGROUND

According to their modified combining rules proposed by Hamada and coworkers[14–16], the core volume v^* and external degrees of freedom c per segment for binary mixtures can be written as:

$$v^* = \phi_1^2 v_1^* + 2\phi_1\phi_2 v_{12}^* + \phi_2^2 v_2^* \tag{1}$$

where

$$v_{12}^* = [(v_1^{*1/3} + v_2^{*1/3})/2]^3 \quad \text{or} \quad v_{12}^* = (v_1^* + v_2^*)/2 \tag{2}$$

and

$$c = \phi_1 c_1 + \phi_2 c_2 - \phi_1 \theta_2 c_{12} \tag{3}$$

respectively, where ϕ_i and θ_i $(i = 1, 2)$ are the segment and site fractions, respectively, of component i, v_i^* is the core volume per segment of component i, and c_{12} is the parameter characterizing the deviation from additivity. Also, random mixing was assumed in the same way as Flory's assumption[8]. On the basis of the above combining rules, we can derive various thermodynamic functions using the partition function proposed by Flory[8].

In this work, for simplicity, it is assumed that the sizes of the core volume per segment for the pure components and their mixture are equal to one another instead of equation (1), that is:

$$v^* = v_1^* = v_2^* \tag{4}$$

Then, the residual chemical potential, $(\mu_1 - \mu_1^\circ)^R$, of component 1, defined by:

$$\mu_1 - \mu_1^\circ = RT[\ln(1-\phi_2) + (1 - r_1/r_2)\phi_2] + (\mu_1 - \mu_1^\circ)^R \tag{5}$$

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can be expressed as:

$$
\begin{aligned}
(\mu_1-\mu_1^\circ)^{\mathrm{R}} = {} & -\tfrac{3}{2}r_1p_1^*v^*\tilde{T}_1\ln(m/m_1)+3r_1RTc_{12}\theta_2^2\ln K \\
& -\tfrac{3}{2}[(m_1-m_2)/m]p^*r_1v^*\tilde{T}\phi_2 \\
& +3p_1^*r_1v^*\tilde{T}_1\ln[\tilde{v}_1^{1/3}-1)/(\tilde{v}^{1/3}-1)] \\
& +3r_1RTc_{12}\theta_2^2\ln(\tilde{v}^{1/3}-1) \\
& +p_1^*r_1v^*(1/\tilde{v}_1-1/\tilde{v})+r_1v^*X_{12}\theta_2^2/\tilde{v}
\end{aligned}
\tag{6}
$$

with

$$K=(2\pi mkT/h^2)^{1/2}(gv^*e^3)^{1/3} \qquad m=\phi_1m_1+\phi_2m_2 \tag{7}$$

where r_i is the number of segments in molecule i, m_i is the mass per segment of component i and X_{12} is the exchange enthalpy parameter. Also, $\tilde{p}$, $\tilde{v}$ and $\tilde{T}$ are the reduced parameters of pressure, volume and temperature, respectively, defined using their reduction parameters p^*, v^* and T^* as follows:

$$\tilde{p}=p/p^* \qquad \tilde{v}=v/v^* \qquad \tilde{T}=T/T^* \tag{8}$$

Finally, g, which is the geometric factor, is taken as $(4/3)2^{1/2}\pi$ under the assumption of the coordination number $z=12$. The reduced and reduction parameters can be obtained from the specific volume v_{sp} or the density ρ, the thermal expansion coefficient α and the thermal pressure coefficient γ using the following equations derived from the equation of state at $p=0$:

$$\tilde{v}^{1/3}=1+\alpha/3(1+\alpha T) \tag{9}$$

$$\tilde{T}=(\tilde{v}^{1/3}-1)/\tilde{v}^{4/3} \tag{10}$$

$$p^*=\gamma T\tilde{v}^2 \tag{11}$$

The interaction parameter χ can be written from equation (5) as follows:

$$\chi=(\mu_1-\mu_1^\circ)^{\mathrm{R}}/(RT\phi_2^2) \tag{12}$$

At infinite dilution:

$$
\begin{aligned}
\chi_1 = {} & \lim_{\phi_2 0\to 0}\chi \\
= {} & 3p_1^*r_1v^*\tilde{T}_1\{m_2/m_1-1)[2(T_1^*p_2^*/T_2^*p_1^*) \\
& -(m_2/m_1+1) \\
& -2(T_1^*/p_1^*)(s_2/s_1)(Rc_{12}/v^*)]/4 \\
& +\ln[K_1(\tilde{v}_1^{1/3}-1)] \\
& \times(s_2/s_1)^2(T_1^*/p_1^*)(Rc_{12}/v^*)\}/RT \\
& +(p_1^*r_1v^*/\tilde{v}_1)(A^2\alpha_1T/2+Y_{12})/RT
\end{aligned}
\tag{13}
$$

where

$$
\begin{aligned}
A = {} & (1-T_1^*/T_2^*)(p_2^*/p_1^*)-(s_2/s_1)(X_{12}/p_1^*) \\
& +(T_1^*/p_1^*)(s_2/s_1)(Rc_{12}/v^*)
\end{aligned}
\tag{14}
$$

and

$$Y_{12}=(s_2/s_1)^2(X_{12}/p_1^*) \tag{15}$$

in which s_2/s_1 is the surface ratio of the segment.

The heat of mixing per segment is:

$$
\begin{aligned}
\Delta H^{\mathrm{M}}/\bar{r}N = {} & -RT(c/\tilde{v}\tilde{T}-\phi_1c_1/\tilde{v}_1\tilde{T}_1-\phi_2c_2/\tilde{v}_2\tilde{T}_2) \\
& -\tfrac{3}{2}RTc_{12}\phi_1\theta_2 \\
= {} & v^*[\phi_1p_1^*(1/\tilde{v}_1-1/\tilde{v})+\phi_2p_2^*(1/\tilde{v}_2-1/\tilde{v}) \\
& +\phi_1\theta_2X_{12}/\tilde{v}]-\tfrac{3}{2}RTc_{12}\phi_1\theta_2
\end{aligned}
\tag{16}
$$

where $\bar{r}N$ is the number of total segments of N_1 r_1-mers and N_2 r_2-mers. The heat of mixing to infinite dilution, $\Delta H^{\mathrm{M}}(\infty)$, can be derived from equation (16) as follows:

$$
\begin{aligned}
\Delta H^{\mathrm{M}}(\infty) = {} & (v_{\mathrm{sp},2}^*/\tilde{v}_1)p_2^*[(T_1^*/T_2^*)-1]\alpha_1T \\
& +v_{\mathrm{sp},2}^*p_2^*(1/\tilde{v}_2-1/\tilde{v}_1) \\
& +(v_{\mathrm{sp},2}^*/\tilde{v}_1)(s_2/s_1)(1+\alpha_1T)X_{12} \\
& -(RTc_{12}v_{\mathrm{sp},2}^*/v^*)(s_2/s_1)(\tfrac{9}{2}+4\alpha_1T)
\end{aligned}
\tag{17}
$$

The ratio of the excess volume V^{E} to the sum v° of the volumes of the pure components is:

$$V^{\mathrm{E}}/v^\circ=\tilde{v}/\tilde{v}_0-1 \tag{18}$$

where

$$\tilde{v}_0=\phi_1\tilde{v}_1+\phi_2\tilde{v}_2 \tag{19}$$

EXPERIMENTAL

Materials

Two samples of polystyrene (PS) with weight-average molecular weights of 9.0×10^3 and 1.75×10^4 ($M_w/M_n<1.06$ for both polymers), purchased from Pressure Chemical Co., were used in this study. The latter sample was used only for measurements of cloud points. Poly(methylphenylsiloxane) (PMPS), supplied by Toray Silicone Co., was dried under vacuum for 40 h at 150°C to eliminate low-boiling substances, followed by fractionation in a water/acetone system. The fraction of PMPS obtained thus was used, and its M_w and M_n determined by the small-angle X-ray scattering method and vapour-pressure osmometry were 1.9×10^3 and 1.3×10^3, respectively.

Blend samples were prepared by two methods: casting from a common solvent (toluene) for the blends containing >50 wt% PS, and mixing of the two polymers without solvent for other blends.

Measurements

Densities ρ and thermal expansion coefficients α for PMPS and PS were determined dilatometrically on the basis of the absolute densities at 25°C. The densities at 25°C were measured with a digital precision densitometer (Shibayama Scientific Co.) for PMPS, and by the sink-and-float method for PS. The liquids used for the sink-and-float measurement were water and 2-chloroethanol, and the densities of their mixture were determined with a pycnometer. Thermal pressure coefficients γ for PMPS were measured according to Flory's method[17] described in previous papers[12,18,19].

Heats of mixing to infinite dilution $\Delta H^{\mathrm{M}}(\infty)$ were measured with a Tian–Calvet microcalorimeter at 125°C, which was above the glass transition temperature. In this measurement, PS was dissolved in liquid PMPS. Excess volumes V^{E} were determined from the densities of the two pure polymers and their mixtures. Their densities were measured by the sink-and-float method described above and with the digital densitometer, for blends containing >50 wt% PS and <50 wt% PS, respectively. Cloud-point curves were determined in the same way as described in the preceding paper[12]. Heating and cooling rates were 0.05–0.1 °C min^{-1}. Thickness of the sample films was about 2 mm.

RESULTS AND DISCUSSION

The results for ρ, α and γ were as follows. For PS with $M_w = 9.0 \times 10^3$:

$$\rho\ (\mathrm{g\,cm^{-3}}) = 1.0850 - 0.605 \times 10^{-3}t + 0.12 \times 10^{-6}t^2 \qquad (90\text{–}150^\circ\mathrm{C})$$

$$\alpha\ (\mathrm{deg^{-1}}) = 5.58 \times 10^{-4} + 7.85 \times 10^{-8}t \qquad (90\text{–}150^\circ\mathrm{C})$$

And for PMPS with $M_w = 1.9 \times 10^3$:

$$\rho\ (\mathrm{g\,cm^{-3}}) = 1.1165 - 0.802 \times 10^{-3}t + 0.932 \times 10^{-6}t^2 - 0.660 \times 10^{-8}t^3 + 0.209 \times 10^{-10}t^4 \qquad (50\text{–}95^\circ\mathrm{C})$$

$$\alpha\ (\mathrm{deg^{-1}}) = 0.7195 \times 10^{-3} - 0.126 \times 10^{-5}t + 0.186 \times 10^{-7}t^2 - 0.792 \times 10^{-10}t^3 \qquad (50\text{–}95^\circ\mathrm{C})$$

$$\gamma\ (\mathrm{bar\,deg^{-1}}) = 12.89 - 5.26 \times 10^{-2}t + 0.85 \times 10^{-4}t^2 \qquad (20\text{–}90^\circ\mathrm{C})$$

where t is the temperature (°C). In *Table 1* are listed the equation-of-state parameters obtained from the above observed values of ρ, α and γ according to Flory's method[8,9], i.e. equations (9)–(11). Here, the value of p^* for PS was evaluated by use of γ measured by Höcker *et al.*[20].

The results of $\Delta H^M(\infty)$ at 125°C and V^E/V° (V° is the total volume of the constituent polymers before mixing) at 50°C are shown in *Table 2* and *Figure 1*, respectively. The value of $\Delta H^M(\infty)$ was positive, i.e. endothermic, in contrast to that for miscible high-molecular-weight polymer blends such as poly(vinyl methyl ether)/polystyrene[12]. Positive heats of mixing have been reported for the oligomer blends of poly(ethylene glycol)/poly(propylene glycol)[21,22] and poly(isobutylene)/poly(dimethylsiloxane)[6].

Table 1 Equation-of-state parameters at 50°C

Sample	v^*_{sp} ($\mathrm{cm^3\,g^{-1}}$)	T^* (K)	p^* ($\mathrm{J\,cm^{-3}}$)
PMPS	0.7766	6712	481
PS	0.8159	7702	528[a]

[a] Obtained by the use of γ measured by Höcker *et al.*[20]

Table 2 Heat of mixing to infinite dilution, $\Delta H^M(\infty)$, at 125°C

Experimental	$2.40 \pm 0.15\ \mathrm{J\,g^{-1}}$
Theoretical[a]	$2.34\ \mathrm{J\,g^{-1}}$

[a] Theoretical value calculated with $X_{12} = 2.3\ \mathrm{J\,cm^{-3}}$ and $c_{12} = -0.003$

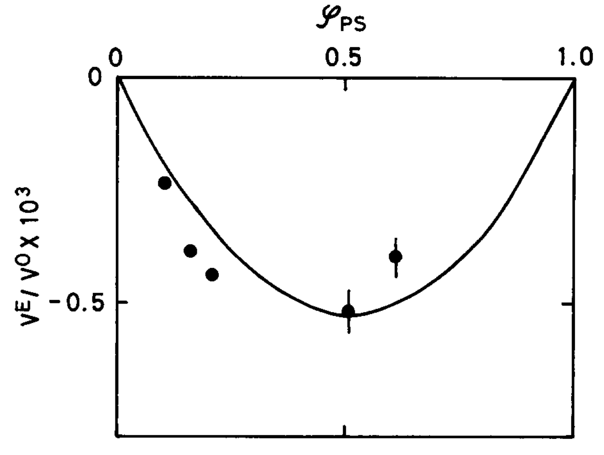

Figure 1 The excess volume ratios V^E/V° for the PMPS/PS ($M_w = 9.0 \times 10^3$) system at 50°C. The full curve is a theoretical curve

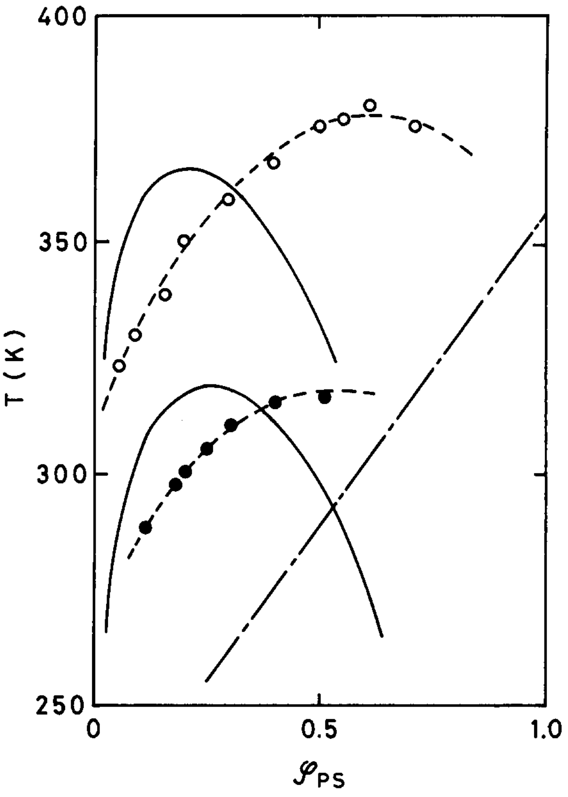

Figure 2 The cloud-point curves. The open circles represent the experimental points for PMPS ($M_w = 1.9 \times 10^3$)/PS ($M_w = 1.75 \times 10^4$) and the full circles for PMPS ($M_w = 1.9 \times 10^3$)/PS ($M_w = 9.0 \times 10^3$). The full curves, corresponding to the respective molecular weights of PS, were calculated with $X_{12} = 2.3\ \mathrm{J\,cm^{-3}}$ and $c_{12} = -0.003$. The chain line represents the glass transition temperature obtained for PMPS ($M_w = 2800$)/PS ($M_w = 9000$) by Nojima *et al.*[24]

In *Table 2* and *Figure 1* are also shown the values calculated from equations (17) and (18), respectively, using the surface ratio $s_2/s_1 = 1.152$ obtained from Bondi's table[23] for the van der Waals radii, the exchange enthalpy parameter $X_{12} = 2.3\ \mathrm{J\,cm^{-3}}$ and the parameter for the external degrees of freedom $c_{12} = -0.003$ together with the equation-of-state parameters at 50°C, where the subscripts 1 and 2 represent the components PMPS and PS, respectively. As shown in *Table 2* and *Figure 1*, the theory gives a good agreement with experiments by use of these values of X_{12} and c_{12}.

Figure 2 shows the cloud-point curves. The curves were the theoretical binodal curves calculated using the above values of X_{12} and c_{12} and the equation-of-state parameters at 50°C. The theory can reproduce fairly well the temperature at the maximum in the experimental cloud-point curves but not its concentration. The location of this concentration observed for the present system does not appear to obey the following equation expressing the critical concentration for mixtures of r_1- and r_2-mers:

$$\phi_{2,\mathrm{cr}} = r_1^{1/2}/(r_1^{1/2} + r_2^{1/2}) \qquad (20)$$

derived from the familiar Flory–Huggins theory[25] under the assumptions of monodispersity and concentration-independent χ parameter. Allen *et al.*[6] observed that the asymmetry in the cloud-point for the *UCST*-type oligomer blends of poly(isobutylene)/poly(dimethylsiloxane) was opposite to that expected from equation (20), namely from the difference between the constituents' molecular weights. Furthermore, the polyisoprene/polystyrene oligomer blends were found to have bimodality or a shoulder in the cloud-point curves[7,26]. Koningsveld *et al.*[7] discussed these remarkable features for the oligomer blends from various points of view, and suggested that they may be due to combinatorial entropy of mixing and to polydispersity of the molecular-weight distribution. Ten Brinke *et al.*[27] also reported that, for *LCST*-type blends of low-molecular-weight isotactic poly(ethyl methacrylate) (i-PEMA) and high-molecular-weight poly(vinylidene fluoride) (PVF_2), the minimum in the cloud-point curve occurred at the PVF_2-rich side of the phase diagram, and that this irregular asymmetry could be explained by introduction of a positive c_{12}. However, X_{12} was negative in that case, namely a specific interaction may be dominant in the i-PEMA/PVF_2 system, while the oligomer systems (including the PMPS/PS system studied here) have a positive X_{12}. At present, it is not clear whether disagreement between the theoretical and experimental maximal points shown in *Figure 2* comes from the equation-of-state theory or from Koningsveld's suggestions. In any event, the irregularity in the cloud-point curve for the oligomer systems needs to be investigated further.

The dependence of χ/r_1 extrapolated to $\phi_{PS}=0$, χ_1/r_1, on temperature was calculated from equation (13) using the above values of X_{12} and c_{12}. As shown in *Figure 3*, χ_1 is positive over all the temperature range and its curve is concave, which corresponds to a positive value of X_{12}. This calculated temperature dependence predicts that *LCST* could appear at about 400°C for blends of PMPS ($M_w=1.9\times10^3$) and PS ($M_w=1.75\times10^4$) if neither chemical structure nor molecular weight of the polymers changed at high temperature.

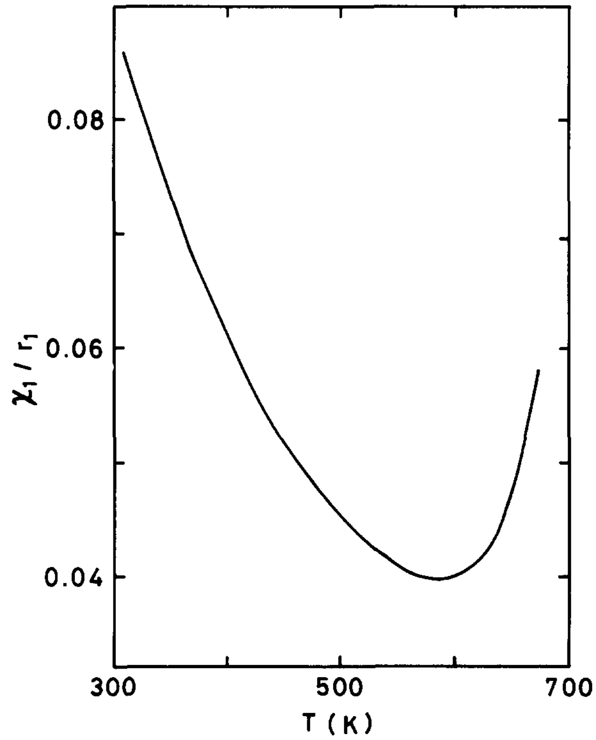

Figure 3 The temperature dependence of the interaction parameter χ_1/r_1 calculated with $X_{12}=2.3\ \mathrm{J\,cm^{-3}}$ and $c_{12}=-0.003$

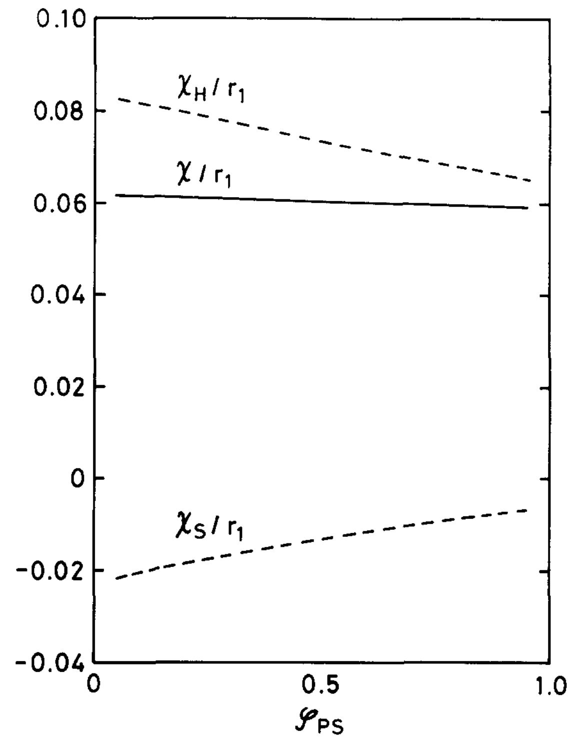

Figure 4 The calculated concentration dependence of χ/r_1, χ_H/r_1 and χ_S/r_1 at 125°C

Figure 4 shows the calculated dependences of χ/r_1, χ_H/r_1 and χ_S/r_1 on concentration at 125°C, where χ_H/r_1 and χ_S/r_1 are defined by:

$$\chi=\chi_H+\chi_S=\Delta H_1^R/RT\phi_2^2-\Delta S_1^R/R\phi_2^2 \qquad (21)$$

χ/r_1 is slightly dependent on concentration, as found for other polymer blends[12,13].

CONCLUSIONS

Blends of the oligomers, PMPS and PS, were endothermic and showed a *UCST*-type phase diagram, as reported so far for other blends containing oligomers. Also, the excess volumes were negative. In the application of the modified Flory equation-of-state theory to this system, the theory reproduced various experimental thermodynamic properties by the use of the positive exchange enthalpy parameter X_{12}, except for the concentration at the maximum in the cloud-point curves.

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