

Thermodynamic Properties of Poly(dimethylsiloxane)-*n*-Alkane Solutions*

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ABSTRACT: Shiomi *et al.* showed from their experimental results that characteristic parameters depend nonlinearly on concentration, and that the size difference between segment and solvent should be reflected by the Flory theory. Their effects are examined in the present report in terms of the solution properties of the PDMS-*n*-alkane system. The concentration dependence of v^* was as expected from Shiomi *et al.*'s theory, but deviations from additivity appeared in P^* , T^* , \bar{v} and $P^*v_{sp}^*/T^*$ (or external degree of freedom). The concentration dependence of χ was overestimated by this modified Flory theory as also by the original Flory theory.

KEY WORDS Thermodynamics / Solution Properties / Characteristic Parameter / Poly(dimethylsiloxane) /

By the new Flory and Patterson theory based on the corresponding states theory^{1,2} it has been possible to interpret the solution properties of polymers such as polyethylene or polystyrene. In our previous study,³ however, we found unexpected deviation from these theories in regard to the solution properties of poly(dimethylsiloxane) (PDMS) or polyisobutylene. These deviations have also been found by other authors.⁴⁻⁶

Shiomi *et al.*⁴ proposed a modification of the Flory theory by expressing the characteristic volume of solution, v^* , as

$$v^* = \sigma_1^2 v_1^* + 2\sigma_1 \sigma_2 v_{12}^* + \sigma_2^2 v_2^*.$$

The obtained values of P^* and P^*/T^* by using the parameters σ_i , and the segment fractions (=core volume fractions) θ_i , served to explain well of the thermodynamic properties and characteristic parameters of solutions. For a positive appraisal of the different size between polymer segment and solvent molecule, PDMS in *n*-alkane solutions were chosen for the present experiment.

EXPERIMENTAL

PDMS KF-96 with 6000 cSt (centistokes) was obtained from Shin-Etsu Chemical Co. It was suf-

ficiently degassed to remove volatile constituents, and low-molecular-weight fractions were removed by fractional precipitation in benzene-methanol. The viscosity-average molecular weight determined from the equation $\log \eta_{\text{cst}}^{25^\circ\text{C}} = 1.00 + 0.0123 \times M^{0.5}$ was found to be 5.10×10^4 . *n*-Alkanes (*n*-hexane, *n*-octane, and *n*-decane) were of reagent grade and used without further purification.

P - V relations at 25°C were measured by a high pressure piston-cylinder cell⁶ at volume intervals of ca. 0.04 cm³ up to 200 bar and rearranged by the Tait equation,

$$V(P, T) = V(O, T) \times [1 - C \cdot \log(1 + P/B)],$$

$$\text{where } B = b_1 \cdot \exp(-b_2 T).$$

Thermal expansion coefficients were measured by a dilatometer connected to a capillary tube to magnify volume changes. The measurements were carried out at every 0.2°C change in the neighborhood of 25°C (total 10 points).

The solution concentrations were determined by weighing the solution and the dry polymer.

THEORETICAL

The equation of state for a solution can be expressed by either the original or modified Flory

theory as

$$\bar{P}\bar{v}/\bar{T} = \bar{v}^{1/3}/(\bar{v}-1) - 1/\bar{v}\bar{T}$$

and the reduced variables can be obtained from experimental data by the relations

$$\bar{v}^{1/3} = 1 + (1/3)\alpha T/(1 + \alpha T)$$

$$\bar{T} = (\bar{v}^{1/3} - 1)/\bar{v}^{4/3}$$

$$P^* = T \cdot \gamma \cdot \bar{v}^2$$

Where α is the thermal expansion coefficient and γ is the thermal pressure coefficient.

In the Flory theory, the concentration dependence of P^* and T^* expressed by

$$P^* = \Phi_1 P_{11}^* + \Phi_2 P_{22}^* - \Phi_1 \Phi_2 X_{12}$$

$$P^*/T^* = \Phi_1 P_{11}^*/T_{11}^* + \Phi_2 P_{22}^*/T_{22}^*$$

$$\Phi_1 \text{ (volume fraction of } r_1\text{-mer)} = 1 - \Phi_2$$

$$= w_1 v_{sp,1}^*/(w_1 v_{sp,1}^* + w_2 v_{sp,2}^*)$$

$$\theta_2 \text{ (segment site fraction of } r_2\text{-mer)} = 1 - \theta_1$$

$$= (s_2/s_1)\Phi_2/\Phi_1 + [s_2/s_1]\Phi_2$$

Here X_{12} is the polymer-solvent interaction parameter, w_i is the weight fraction of an r_i -mer, and v_{sp}^* is the specific characteristic volume. Molecular size was estimated by the Prigogine equation, $3cr = 2r + 1 = MP^*v_{sp}^*/RT$, where M is the molecular and $3cr$ is the external degree of freedom per molecule.

The characteristic volume parameters in the modified Flory theory are expressed by

$$v^* = \sigma_1^2 v_1^* = 2\sigma_1 \sigma_2 v_{12}^* + \sigma_2^2 v_2^*$$

$$v_{12}^* = \zeta(v_1^{*1/3} + v_2^{*1/3})/8$$

$$\zeta = 1 \text{ for hard sphere}$$

and P^* and P^*/T^* can be expressed in terms of these parameters as,

$$P^* = \sigma_1 \theta_1 P_{11}^*(v_1^*/v^*)^2 + \sigma_2 \theta_2 P_{22}^*(v_2^*/v^*)^2$$

$$+ 2\sigma_1 \theta_2 P_{12}^*(v_{12}^*/v^*)^2 \quad (1)$$

$$P^*/T^* = \sigma_1 P_{11}^*(v_1^*/v^*)/T_{11}^* + \sigma_2 P_{22}^*(v_2^*/v^*)/T_{22}^* - \sigma_1 \theta_2 \delta (v_{12}^*/v^*) \quad (2)$$

where σ_2 (segment fraction) = $1 - \sigma_1$

$$= N_2 r_2 / (N_1 r_1 + N_2 r_2)$$

N_i : number of molecules of r_i -mer

The interaction energy between segment and solvent molecules is expressed as P_{12}^* in the last term in eq 1.

In eq 2, the parameter δ represents the deviation of external degree of freedom from additivity as

$$c = \sigma_1 c_1 + \sigma_2 c_2 - \sigma_1 \theta_2 v_{12}^* \delta / k$$

This parameter corresponds to Q_{12} in the original Flory theory, the entropy correction term, but Q_{12} has a less definite physical meaning, and shows a large negative value for a PDMS solution in benzene.⁷

In the expression of X_{12} ,⁷ the term $v_{12}^* \delta \theta_2^2 \times \log(\bar{v}_1^{1/3} - 1)$ corresponds to $v_1^* Q_{12} \theta_2^2$ in the Flory theory, and the concentration dependence of $\log(\bar{v}_1^{1/3} - 1)$ amount to 8% at $\Phi_2 = 1$. This large concentration dependence also appears in χ of the modified Flory theory.

RESULTS AND DISCUSSION

The values of the characteristic parameters in the original and modified Flory theories were calculated by Sugiyama's results,⁸ and are shown in Table I. The reasons for adopting his results are; (1) the value of s_2/s_1 well accounts for the solution properties of PDMS in benzene, cyclohexane, and ethyl butyl ketone,^{3,4,6,7} (2) the concentration dependence of χ is well expressed by these values.⁸

Equation of state parameters are shown in Tables II, III, and IV, and the concentration dependence of characteristic parameters, reduced volume, v^E/v^0 , $P^*v_{sp}^*/T^*$ and χ is shown in Figures 1-7.

Table I. Parameters for the calculation of thermodynamic quantities for PDMS-*n*-octane

$X_{12}/J \text{ cm}^{-3}$	s_2/s_1	$P_{12}^*/J \text{ cm}^{-3}$	$10^3 \delta$	ζ	$\Delta H_M^\infty / J \text{ g}^{-1}$		$10^3 v^E/v^0$	
					Exptl	Calcd	Exptl	Calcd
4.01	0.83	420	1.8	1	2.56	4.25	0.38	1.20

Thermodynamic Properties of PDMS Solutions

Table II. Equation-of-state parameters for PDMS-(n -C₆) at 25°C

	n -C ₆	1/8	1/4	1/2	1/1	PDMS
w_2	0	.1500	.2980	.5378	.7480	1
v_2	0	.1065	.2229	.4401	.6673	1
ϕ_2	0	.1136	.2357	.4580	.6831	1
$10^3\alpha$	1.385	1.309	1.254	1.135	1.050	0.9070
$\bar{v}^{1/3}$	1.097	1.093	1.091	1.084	1.080	1.071
\bar{v}	1.322	1.308	1.298	1.275	1.258	1.228
\bar{T}	0.6717	0.6543	0.6410	.06097	.05852	.05394
$\bar{v}/\text{cm}^3 \text{g}^{-1}$	1.527	1.452	1.379	1.260	1.156	1.031
T^*/K	4439	4557	4652	4890	5095	5528
$10^4\beta/1 \text{ bar}^{-1}$	1.701	1.621	1.553	1.431	1.336	1.196
$\gamma/\text{bar K}^{-1}$	8.143	8.075	8.075	7.929	7.857	7.583
P^*/bar	4241	4118	4054	3841	3706	3411
P^*v^*/T^*	1.104	1.004	0.926	0.776	0.668	0.518

Table III. Equation-of-state parameters for PDMS-(n -C₈) at 25°C

	n -C ₈	1/4	2/4	3/4	4/4	PDMS
w_2	0	.2561	.4577	.6586	.8322	1
v_2	0	.1986	.3779	.5814	.7812	1
ϕ_2	0	.2052	.3877	.5914	.7882	1
θ_2	0	.1771	.3454	.5467	.7562	1
$10^3\alpha$	1.159	1.098	1.049	0.9971	0.9580	0.9070
$\bar{v}^{1/3}$	1.086	1.082	1.079	1.076	1.074	1.071
\bar{v}	1.279	1.267	1.258	1.247	1.239	1.228 ₂
\bar{T}	.06162	.05992	.05850	.05690	.05565	.05394
$\bar{v}/\text{cm}^3 \text{g}^{-1}$	1.432	1.330	1.249	1.169	1.099	1.0312
T^*	4839	4976	5097	5240	5358	5528
v^*	1.119	1.049	0.9933	0.9371	0.8868	0.8395
$10^4\beta/1 \text{ bar}^{-1}$	1.305	1.273	1.250	1.227	1.213	1.196
$\gamma/\text{bar K}^{-1}$	8.880	8.622	8.392	8.126	7.898	7.583
P^*/bar	4333	4129	3958	3768	3615	3411
P^*v^*/T^*	1.003	0.870	0.771	0.674	0.598	0.518

Table IV. Equation-of-state parameters for PDMS-(n -C₁₀) at 25°C

	n -C ₁₀	1/4	2/4	3/4	4/4	PDMS
w_2	0	.2247	.4417	.6171	.7860	1
v_2	0	.1784	.3721	.5469	.7334	1
ϕ_2	0	.1819	.3776	.5528	.7380	1
$10^3\alpha$	1.050	1.023	0.9940	0.9701	0.9466	0.9070
$\bar{v}^{1/3}$	1.080	1.078	1.076	1.075	1.073	1.071
\bar{v}	1.258	1.253	1.247	1.242	1.237	1.228
\bar{T}	.05852	.0577	.05681	.05604	.05528	.05394
$\bar{v}/\text{cm}^3 \text{g}^{-1}$	1.377	1.300	1.225	1.166	1.106	1.031
T^*/K	5095	5166	5349	5320	5294	5528
$v^*/\text{cm}^3 \text{g}^{-1}$	1.095	1.038	0.9830	0.9394	0.8941	0.8395
$10^4\beta/1 \text{ bar}^{-1}$	1.109	1.120	1.133	1.149	1.168	1.196
$\gamma/\text{bar K}^{-1}$	9.464	9.136	8.773	8.443	8.105	7.583
P^*/bar	4464	4273	4064	3880	3695	3411
P^*v^*/T^*	0.959	0.858	0.761	0.685	0.613	0.518

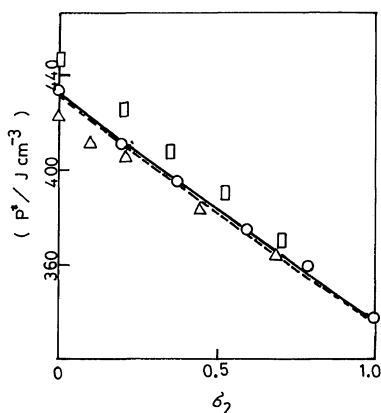


Figure 1. Characteristic pressure vs. concentration curve for PDMS-*n*-hexane (Δ), *n*-octane (\circ) and *n*-decane (\square) at 25°C under atmospheric pressure. Solid curve was made by the Flory theory, and dashed curve, by the modified Flory theory for C_8 . Marks and experimental conditions are the same as in Figures 1 to 7.

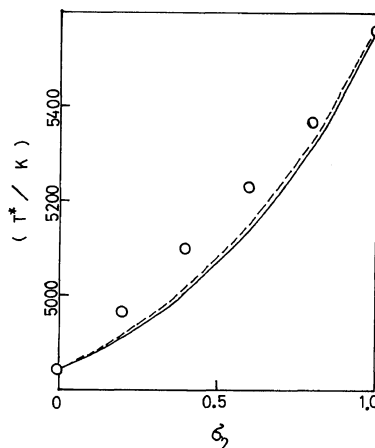


Figure 3. Characteristic temperature vs. concentration curve.

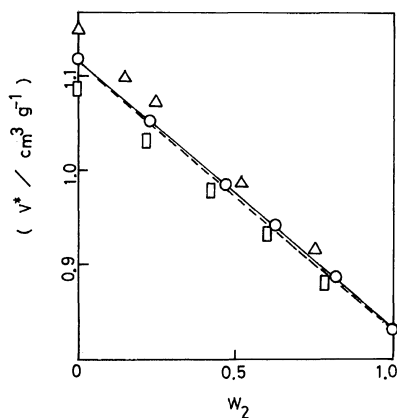


Figure 2. Characteristic specific volume vs. concentration curve.

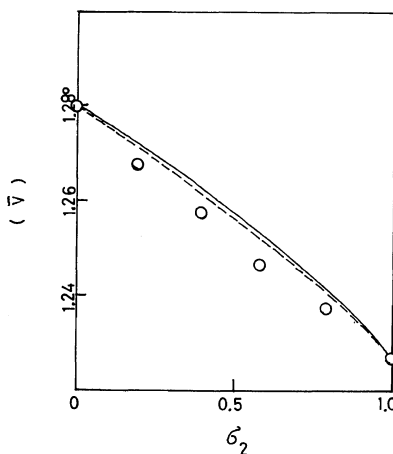


Figure 4. Reduced volume vs. concentration curve.

Characteristic pressures show a slight deviation from additivity, which corresponds to a positive value of X_{12} , and the experimental results are well expressed by the prediction of the original and modified Flory theories.

Additivity for v^* better holds for the solution in *n*-alkane than that in benzene,^{3,7} in which the experimental values lie between the values of the original and modified Flory theories. This would be due to the fact that the ratio of segment sizes is nearly equal to 1 for the solution in *n*-alkane.

Rather large deviations in the two theories from

experimental values were found for T^* or \bar{v} , but a slightly better prediction was made by the modified theory. In the case of PDMS-benzene solution,⁶ the concentration dependence of \bar{v} could be well interpreted by the modified theory, but in the present case the calculated values were larger and the origin of this deviation is not clear.

The external degree of freedom or $P^*v_{sp}^*/T^*$ deviates from additivity. Patterson⁹ assumed that the external degree of freedom decreased by the orientation effect, and predicted a positive deviation from additivity. Our present experimental results, however, displayed a negative deviation but if we

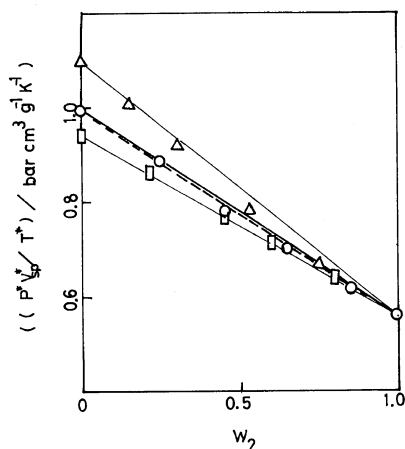


Figure 5. $P^*v_{sp}^*/T^*$ vs. weight fraction curve. ($P^*v_{sp}^*/T^*$ is proportional to the external degree of freedom for each unit mass.)

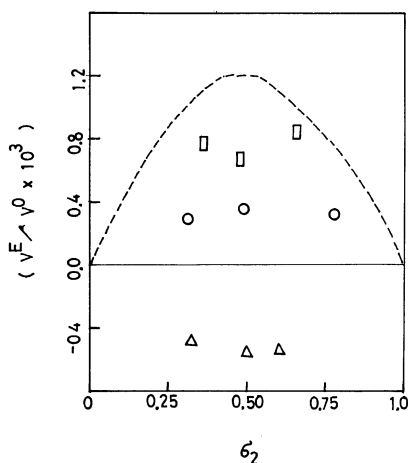


Figure 6. Excess volume of PDMS-*n*-alkane solutions. Dashed curve represents the prediction of the modified Flory theory for PDMS-*n*-octane.

extrapolate our results from *n*-C₆ to *n*-C₈ and *n*-C₁₀, a positive deviation may be expected.

The experimental value of v^E/v^0 was found to be 0.83×10^{-3} at $\phi_2=0.5$ for *n*-octane. This is consistent with 1.20×10^{-3} obtained from the modified Flory theory at this concentration, but markedly different values from the figure were found by the original Flory theory, which might be due to the overestimation of \bar{v} . As a whole, only poor predictions were obtained for \bar{v} , and even for its sign, at each concentration except for the above one.

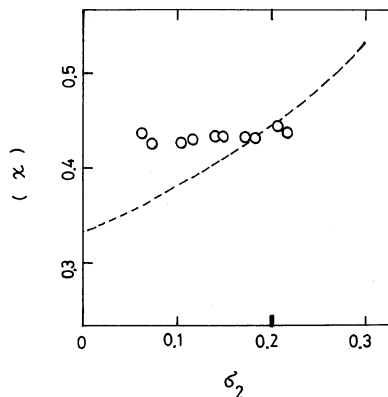


Figure 7. Reduced residual chemical potential χ plotted against segment fraction for PDMS-*n*-octane. Open circles show the results of Sugiyama *et al.* at 25°C. Dashed curve was made by the modified Flory theory obtained from parameters listed in Table I.

Patterson *et al.*² examined the concentration dependence of χ using the value of s_2/s_1 shown in Table I, and found that a large concentration dependence of χ followed with a too large value of X_{12} . If the segment volumes of all components are set equal, P_{12}^* is related to X_{12} by the modified Flory theory as follows:

$$P_{12}^* = P_1^* + (s_1/s_2)P_2^* - X_{12}$$

The value of P_{12}^* calculated from this relationship for *n*-octane is 419 which is very close to 420 in Table I.

In the present paper, we estimate the segment volume of the solvent (*n*-alkane) by the Prigogine theory, based on the short-range intramolecular interactions, and this may influence the concentration dependence of χ . But, the modified Flory theory well explains the relations between the concentration dependence of the characteristic parameters and the thermodynamic properties of solutions in our present case.

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