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Thermodynamics of Solutions of Poly(dimethylsiloxane). 2. Solution of Poly(dimethylsiloxane) in Octamethylcyclotetrasiloxane

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ABSTRACT: The expression for the combinatorial entropy proposed by Prausnitz et al. was examined for a system whose surface ratio is close to unity. For this purpose, osmotic pressures and heats of mixing to infinite dilution were measured for solutions of poly(dimethylsiloxane) in its cyclic oligomer octamethylcyclotetrasiloxane. Interaction parameters χ determined from the osmotic pressures are in disagreement with those calculated according to Flory's polymer solution theory. Volume changes on mixing were also measured. The difference between the value calculated from the Flory theory and the observed value is small.

A new polymer solution theory proposed by Flory[1,2] has semiquantitatively explained various thermodynamic properties of polymer solutions. His theory contains a parameter Q_{12} of uncertain origin. It has been reported that the contribution of Q_{12} to the interaction parameter χ is large for poly(dimethylsiloxane) (PDMS) solutions.[4-7]

Prausnitz et al.[8,9] tried to explain the large values of the Q_{12} term for PDMS solutions by correcting the combinatorial entropy for the bulkiness of the PDMS molecules. Their combinatorial entropy depends on the ratio of the surface area for the polymer segment to that of the solvent segment. It was found that the parameter Q_{12} was not needed for PDMS systems with small surface ratios, where the value of the correction term is large, when their expression for the combinatorial entropy was used.[7,9] It is desirable, therefore, to apply their expression to systems with large surface ratios, where the correction term is small and where recourse to Q_{12} in the Flory theory should be unnecessary.

In this paper, we apply the expression for the combinatorial entropy derived by Prausnitz et al. to a system having a large surface ratio, the PDMS–octamethylcyclotetrasiloxane (OMCTS) system. For this purpose, chemical potentials, excess volumes, and heats of mixing to infinite dilution were measured. Densities, thermal expansivities, and thermal pressure coefficients of OMCTS were also measured to evaluate the thermodynamic quantities of solutions according to the Flory theory.

Experimental Section

Three samples of PDMS were supplied by Shin-Etsu Chemical Co. Two samples with viscosity-average molecular weights of 130 000 and 80 000 were used for measurements of osmotic pressures, and the other sample with M_v = 15 000 was used for volume changes on mixing. The sample with M_v = 80 000 was also used for measurements of heats of mixing to infinite dilution. OMCTS was a gift of A. Muramoto, and impurities were not detected by chromatography. In calorimetric measurements, OMCTS was purified by shaking with mercury, followed by distillation.

Details of the procedures for experimental measurements are described in the preceding paper.[7]

Results

The density ρ of OMCTS as measured with pycnometers was 0.9503 g cm^{-3} at 25.0 °C. The relative densities were converted to absolute values on the basis of the density at 25.0 °C. The least-squares biquadratic equation fitted to the results is

$$\rho\ (\text{g cm}^{-3}) = 0.9776 - 0.1107 \times 10^{-2}t + 0.433 \times 10^{-6}t^2 + 0.606 \times 10^{-8}t^3 - 0.185 \times 10^{-9}t^4 \quad (1)$$

which is accurate to within $\pm 0.5 \times 10^{-4}$ g cm^{-3} in the range 20–61 °C. The values calculated from eq 1 are in good agreement with those obtained by Hürd[10] in a relatively low temperature range. Hunter et al.[11] reported ρ = 0.9497 g cm^{-3} at 25 °C, and Patnode and Wilcock[12] gave ρ = 0.9558 g cm^{-3} at 20 °C.

The thermal expansivity obtained from eq 1 is given by

$$\alpha\ (\text{deg}^{-1}) = 1.138 \times 10^{-3} - 0.125 \times 10^{-7}t - 0.119 \times 10^{-7}t^2 + 0.767 \times 10^{-9}t^3 \quad (2)$$

The thermal pressure coefficients γ were determined at six temperatures in the range 23–61 °C. For each measurement, the temperature dependence of pressure was linear over the measured pressure range. The results are

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Table I
Thermal Pressure Coefficients for OMCTS

t, °C	γ, bar deg^{-1} obsd	calcd	obsd − calcd
23.04	7.906	7.869	0.037
24.31	7.697	7.754	−0.057
30.30	7.337	7.257	0.080
39.52	6.603	6.646	−0.043
54.84	6.089	6.046	0.043
61.24	5.949	5.948	0.001

shown in Table I. From them, γ is obtained by least squares

$$\gamma\ (\text{bar deg}^{-1}) = 10.58 - 0.143t + 0.110 \times 10^{-2}t^2 \quad (3)$$

The mean deviation of the values calculated according to eq 3 from the observed results is 0.041 bar deg^{-1}.

Table II shows the equation-of-state data obtained from eq 1–3 at 25 °C, together with the reduced and characteristic parameters determined according to Flory's theory. In the table, the values for PDMS measured by Shih and Flory[13] and those for decamethyltetrasiloxane (DMTS) measured by Chang and Flory[14] are also included for comparison with those for OMCTS. The specific characteristic volume v_{sp}^* of the ring molecule of OMCTS is smaller than that of the linear molecule of DMTS because of the compactness of the ring molecule. The reduced volume $\tilde{v}$, which reflects the free volume of OMCTS, is a little smaller than that for DMTS. This is similar to the relation between the cyclohexane and *n*-hexane molecules.[15] The values of p^* related to the intermolecular energy are similar for DMTS, OMCTS, and PDMS because all of these molecules have dimethylsiloxane groups.

The heat of mixing $\Delta H^M(\infty)$ to infinite dilution measured at 25 °C was −0.4 ± 0.1 J g^{-1}. Delmas, Patterson, and Böhm[16] obtained a similar result for solutions of PDMS in linear dimethylsiloxane tetramer: $\Delta H^M(\infty) = -0.45$ J g^{-1} at 25 °C.

The excess volume was obtained from specific volumes of the polymer, solvent, and solution measured at 25 °C

$$V^E/V^0 = v_{sp,soln}/(w_1 v_{sp,1} + w_2 v_{sp,2}) - 1 \quad (4)$$

w_i is the weight fraction of component i (i = 1, 2), and V^0 is the sum of the volumes for both components. As shown in Figure 1, the results are negative and the absolute values are very small.

Adopting the combinatorial entropy derived by Flory[17] and Huggins,[18] we can obtain the interaction parameter χ from the osmotic pressure π through the chemical potential

$$(\mu_1 - \mu_1^0)/RT = -\pi V_1^0/RT = \ln(1 - \varphi_2) + (1 - 1/r)\varphi_2 + \chi\varphi_2^2 \quad (5)$$

R is the gas constant, V_1^0 the molar volume of solvent, r the ratio of the number of segments of the polymer to that of the solvent, and φ_2 the segment fraction of polymer defined by Flory:

$$\varphi_2 = w_2 v_{sp,2}^*/(w_1 v_{sp,1}^* + w_2 v_{sp,2}^*) \quad (6)$$

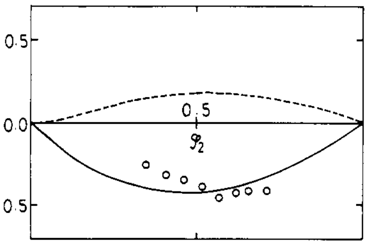

Figure 1. Excess volume V^E/V^0 vs. the segment fraction φ_2 for the PDMS–OMCTS system at 25 °C. The circles are the experimental results. The solid curve was calculated so as to match the experimental values; a negative value of X_{12} was used, as described in the text. The dashed curve was calculated with X_{12} = 0.

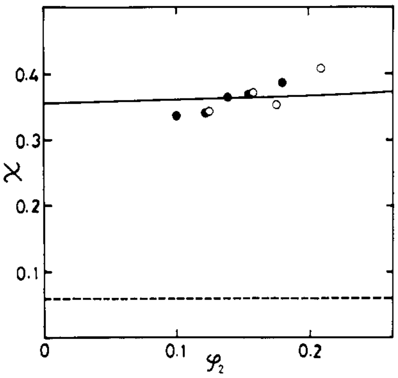

Figure 2. Interaction parameter χ vs. the segment fraction φ_2 for the PDMS–OMCTS system at 25 °C: (○) M_v = 80 000; (●) M_v = 130 000. The experimental results are obtained by eq 5. The dashed curve is calculated according to the Flory theory with X_{12} = 0 and Q_{12} = 0, and the solid curve is calculated with X_{12} = 0 and Q_{12} = −0.0122 J cm^{-3} deg^{-1}.

Values of χ at 25 °C are presented in Figure 2. The value of χ_1, extrapolated to infinite dilution, is close to those for the PDMS–dimer[6,14] and PDMS–trimer[14] systems, but the concentration dependence of χ is different.

Discussion

To examine the combinatorial entropy proposed by Prausnitz et al.,[8,9] we first evaluated the theoretical values of χ. According to Flory's theory,[1-3] χ is given by eq 7* and 9*. (Hereafter, equation numbers referring to the preceding paper are shown with a superscript asterisk.) The value of s_2/s_1 was estimated as 0.91 by approximating an OMCTS molecule as a sphere of radius 6.7 Å and a PDMS molecule as a cylinder of diameter 6.7 Å with a repeating length of 2.9 Å. The value of X_{12} obtained from $\Delta H^M(\infty)$ is −0.13 J cm^{-3}, a negative value, although the absolute value is very small. X_{12} should not be negative in Flory's theory. When we take X_{12} = 0, because of the equality of the chemical nature of the PDMS and OMCTS molecules, $\Delta H^M(\infty)$ is −0.30 J g^{-1}, which is within the experimental error. Therefore, we adopt X_{12} = 0. The concentration dependence of χ, calculated from eq 7* and 9* with Q_{12} = 0, is shown by the broken line in Figure 2. Calculated values of χ are much different from those obtained experimentally. Agreement between the calculated

Table II
Comparison of Equation-of-State Parameters at 25 °C

	v_{sp}, cm^3 g^{-1}	$10^3\alpha$, deg^{-1}	γ, J cm^{-3} deg^{-1}	$\tilde{v}$	v_{sp}^*, cm^3 g^{-1}	T^*, K	p^*, J cm^{-3}
OMCTS	1.0524	1.142	0.769	1.2762	0.8247	4874	374
DMTS[a]	1.1970	1.171	0.700	1.2818	0.9198	4812	343
PDMS[b]	1.0312	0.907	0.758	1.2283	0.8395	5528	341

[a] Reference 14. [b] Reference 13.

and observed values, as shown by the solid curve in Figure 2, requires $Q_{12} = -0.0122$ J cm^{-3} deg^{-1}. (The contribution of Q_{12} to χ_1 is 0.298. This value is close to those for PDMS solutions in the dimer and trimer.[6,14])

The chemical potential with the combinatorial entropy proposed by Prausnitz et al. is given by eq 12*. Their expression contains a correction for molecular bulkiness, the third term in eq 12*. q/r can be identified with s_2/s_1 in Flory's theory. In this system, therefore, q/r was taken as 0.91, and $\alpha^{(t)}$ values were estimated from the bond angles, bond lengths, and characteristic volumes according to the method of Prausnitz et al.[9] The experimental values of χ, obtained from eq 12*, are smaller by only about 0.05 than those obtained from eq 5. Therefore, the observed values of χ remain far from the theoretical values calculated from eq 7* and 9*. In this system, their correction of the combinatorial entropy fails to explain the Q_{12} term in Flory's theory. The correction term may depend too strongly on the surface ratio q/r.

The value of V^E/V^0 calculated from the Flory theory is $+0.18 \times 10^{-3}$ at $\varphi_2 = 0.5$. Although the discrepancy between the calculated and observed values is small, the sign is opposite. Chang and Flory also determined V^E/V^0 for mixtures of PDMS and hexamethyldisiloxane. Both observed and calculated values are negative and larger than that for mixtures of PDMS and OMCTS.

Although the Flory–Huggins combinatorial entropy may overestimate the "true" combinatorial entropy, the correction of the combinatorial entropy cannot alter the differences between the observed and theoretical excess volumes. As an explanation of the discrepancies of the excess volume and χ for the PDMS solutions, Flory and Shih[4] pointed out that the irregularity of the form of the PDMS chain in bulk might be relaxed by solvent molecules. Another source of the disagreement may come from the large free volume of the PDMS molecule compared with that of other polymer molecules.[19,20] The large free volume of the polymer molecules may easily affect packing between polymer and solvent molecules. Renuncio and Prausnitz[21] and Brandani[22] proposed an approximation for nonrandomness, but no clear conclusions about the source of the discrepancies of χ and excess volume were obtained. The discrepancies of χ and excess volume should be considered on the same grounds; further investigations about the combining rules on mixing assumed by Flory are desirable. This will be discussed in subsequent papers.[23,24]

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