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quired for the oxidative coupling to occur.

Conclusions

The results presented in this study demonstrate the significant effect of the polymeric environment on the exciplex structure and excited-state dynamic processes. In particular spectral data suggest that charge delocalization between nearby chromophores in the polymer chain is an inherent feature of exciplex structure in the PVCz–DMT system. The intrachain ring interactions in the polymer system inhibit carbazole triplet formation resulting from exciplex deactivation and may also inhibit the oxidative coupling between polymeric carbazole cation radicals. We anticipate that incorporation of chromophores into a polymeric backbone may prove a useful method of controlling excited-state processes and directing them to preferred pathways.

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Thermodynamics of Solutions of Poly(dimethylsiloxane). 1. Solutions of Poly(dimethylsiloxane) in Methyl Ethyl Ketone, Methyl Isobutyl Ketone, Ethyl *n*-Butyl Ketone, and Diisobutyl Ketone

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ABSTRACT: Osmotic pressure, heats of mixing to infinite dilution, and volume changes on mixing were measured for mixtures of poly(dimethylsiloxane) with four solvents: methyl ethyl ketone, methyl isobutyl ketone, ethyl *n*-butyl ketone, and diisobutyl ketone. The expression for the combinatorial entropy of mixing, containing a correction for molecular bulkiness proposed by Prausnitz et al., was examined for these systems with comparatively small surface ratios, where the value of the correction term is large. The interaction parameters χ determined from osmotic pressure data were in agreement with theoretical values calculated according to Flory's new polymer solution theory; the exchange entropy parameter Q_{12} in the Flory theory, whose physical meaning is obscure, was not necessary. When the Flory–Huggins combinatorial entropy was used, a large value of Q_{12} was necessary to obtain agreement between the observed and calculated values of χ. The excess volume calculated from the Flory theory deviated considerably from the observed values in these systems.

Polymer solution theories based on the corresponding-states principle have successfully represented the thermodynamic properties of polymer solutions. These theories have enabled us to interpret the physical meaning of a lower critical solution temperature and to express volume changes on mixing. Patterson et al.[1,2] explained these phenomena on the basis of the Prigogine theory.[3,4] However, their theory, which employs a Lennard-Jones 6–12 potential, includes parameters difficult to determine and hence has a limitation in comparison with experiments for polymer solutions. The Flory theory[5,6] is expressed by such measurable parameters as thermal expansivities and thermal pressure coefficients. Therefore, the Flory theory has been applied to many polymer solutions.

Although the Flory theory can reproduce thermodynamic properties of polymer solutions, there remain some problems. One of them is the exchange entropy parameter Q_{12}.[7] This parameter is related only to the interaction

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Table I
Densities, Thermal Expansivities, and Thermal Pressure Coefficients[a]

	temp range, °C
MIBK	
$\rho = 0.8160_6 - 0.6257 \times 10^{-3}t - 0.1110 \times 10^{-4}t^2 + 0.2051 \times 10^{-6}t^3 - 0.1465 \times 10^{-8}t^4$	15–55
$\alpha = 0.7555 \times 10^{-3} + 0.2925 \times 10^{-4}t - 0.7832 \times 10^{-6}t^2 + 0.7542 \times 10^{-8}t^3$	
$\gamma = 12.00 - 8.50 \times 10^{-2}t + 1.94 \times 10^{-4}t^2$	20–50
EBK	
$\rho = 0.8341 - 0.829 \times 10^{-3}t - 0.548 \times 10^{-6}t^2 + 0.188 \times 10^{-8}t^3 - 0.137 \times 10^{-11}t^4$	20–60
$\alpha = 0.9693 \times 10^{-3} + 0.446 \times 10^{-5}t - 0.64 \times 10^{-7}t^2 + 0.5 \times 10^{-9}t^3$	
$\gamma = 13.01_2 - 9.320 \times 10^{-2}t + 5.914 \times 10^{-4}t^2$	10–46
DIBK	
$\rho = 0.8223 - 0.806 \times 10^{-3}t + 0.449 \times 10^{-6}t^2 - 0.900 \times 10^{-8}t^3$	15–65
$\alpha = 0.9819 \times 10^{-3} - 0.284 \times 10^{-6}t + 0.369 \times 10^{-7}t^2$	
$\gamma = 10.43 - 3.998 \times 10^{-2}t + 6.824 \times 10^{-5}t^2$	15–52

[a] Units: ρ, g cm^{-3}; α, deg^{-1}; γ, bar deg^{-1}; t, °C.

parameter χ, and the value of Q_{12} has been taken arbitrarily. Although the contribution of the Q_{12} term to χ was determined to be small or negligible for polystyrene[8–11] and polyisobutylene solutions,[12–18] it was found by Flory and Shih[19] to be unusually large for poly(dimethylsiloxane) (PDMS) solutions in benzene, chlorobenzene, and cyclohexane. Sugamiya et al.[20] and Chahal et al.[21] also found large values of Q_{12} for other PDMS systems. Prausnitz et al.[22,23] tried to explain this large value of Q_{12} by a combinatorial correction for the bulkiness of the PDMS molecules. Their expression for the combinatorial entropy depends on the ratio of the surface area of the polymer segment to that of the solvent segment, and the magnitude of the correction increases as the surface ratio decreases.

Another problem is that the Flory theory cannot reproduce the observed values of excess volume for some PDMS systems.[19]

In this paper, we examine the combinatorial entropy proposed by Prausnitz et al. for PDMS systems with comparatively small surface ratios, where the correction term is large. (A system with a large surface ratio, where the correction term is small, is discussed in part 2.) For this purpose, we measured osmotic pressures and heats of mixing to infinite dilution for mixtures of PDMS with four solvents: methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), ethyl *n*-butyl ketone (EBK), and diisobutyl ketone (DIBK). The examination is made by comparing the values of χ obtained from osmotic pressures with those calculated according to the Flory theory. The exchange parameters X_{12} and Q_{12} in the Flory theory are discussed in the process of evaluation of the theoretical values of χ. We also measured excess volumes for the above four systems and compared them with those calculated from the Flory theory. For these purposes, thermal expansivities and thermal pressure coefficients for MIBK, EBK, and DIBK were measured.

Experimental Section

Two samples of PDMS were obtained by crude fractionation from a commercial PDMS manufactured by Shin-Etsu Chemical Co. A sample with a viscosity-average molecular weight of 80 000 was used for measurements of osmotic pressures and heats of mixing to infinite dilution, and another sample with $M_v = 15\,000$ was used for measurements of excess volume. Chromatoquality or spectroquality MEK was used without further purification; other solvents were dried over potassium carbonate and fractionally distilled. In calorimetric measurements, each solvent was purified by shaking with mercury, followed by distillation.

Densities were determined from relative densities measured dilatometrically at intervals of ca. 2 °C on the basis of absolute values measured with pycnometers or a digital precision densitometer manufactured by Shibayama Scientific Co. Thermal expansivities were obtained from the densities. Thermal pressure coefficients were determined by a method similar to that used by Orwoll and Flory.[24] Pressures were measured with a dead-weight pressure gauge manufactured by Budenberg Gauge Co.

Osmotic pressures were measured with a high-pressure osmometer similar to that used by Eichinger and Flory.[7] Schleicher and Schüll membranes 08 were used. They were conditioned according to the conventional procedure. Heats of mixing to infinite dilution were measured with a Tian-Calvet microcalorimeter. Volume changes on mixing were determined from the densities of solute, solvent, and solution measured with the digital densitometer.

Results and Discussion

Equation-of-State Parameters for Pure Components. The density ρ and the thermal expansivity α are represented by polynomials in powers of the Celsius temperature t (Table I). The range of error in ρ is ±0.0001 g cm^{-3} for each solvent. Table I also shows the thermal pressure coefficient γ. The mean deviations of calculated γ from the experimental values are in the range 0.053–0.042 bar deg^{-1} for three solvents. Table II shows the values of the specific volume v_{sp}, α, and γ calculated from the equations in Table I at selected temperatures. The values for MEK and PDMS are cited from Flory and Höcker[8] and Shih and Flory,[25] respectively.

According to Flory's theory,[5,6] based on the corresponding-states principle, we can obtain the reduced variables and the characteristic parameters from

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

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \quad (2)$$

$$p^* = \gamma T \tilde{v}^2 \quad (3)$$

where $\tilde{v}$ and $\tilde{T}$ are the reduced volume and reduced temperature, respectively, and defined by $\tilde{v} = v/v^*$ and $\tilde{T} = T/T^*$. Here v^*, T^*, and p^* are the characteristic volume, temperature, and pressure, respectively. The characteristic and reduced parameters are shown in Table II. The values of $\tilde{v}$, which are related to the free volume, are smallest for DIBK and largest for MEK.

Thermodynamic Properties of Solutions. The results of heats of mixing $\Delta H^M(\infty)$ to infinite dilution for the four systems are shown in Table III. The value of $\Delta H^M(\infty)$ measured for the PDMS–MEK system at 35 °C by Morimoto[26] is 10.8 J cm^{-3}, and the value at 30 °C by Bianch et al.[27] is 14.2 J g^{-1}. Our result is in very good agreement with the latter, while Morimoto's result is somewhat lower. For each system, the heats of mixing to infinite dilution are endothermic and the temperature dependence is very small in the temperature range considered here. The value

Table II
Equation-of-State Parameters

t, °C	v_{sp}, cm³ g⁻¹	$10^3\alpha$, deg⁻¹	γ, J cm⁻³ deg⁻¹	$\tilde{v}$	v_{sp}^*, cm³ g⁻¹	T^*, K	p^*, J cm⁻³
			MEK[a]				
20	1.2421	1.291	1.184	1.3004	0.9552	4547	587
35	1.2669	1.340	1.072	1.3216	0.9586	4588	577
50	1.2932	1.389	1.006	1.3428	0.9631	4635	586
			MIBK				
20	1.2492	1.088	1.038	1.2617	0.9901	4960	484
35	1.2704	1.143	0.9263	1.2838	0.9896	4951	470
			EBK				
35	1.2430	1.068	1.047	1.2686	0.9798	5127	519
50	1.2634	1.095	0.9831	1.2848	0.9833	5180	524
			DIBK				
35	1.2590	1.017	0.9114	1.2581	1.0007	5261	444
			PDMS[b]				
20	1.0265	0.905	0.780	1.2248	0.8381	5494	343
35	1.0406	0.909	0.716	1.2354	0.8423	5596	337
50	1.0549	0.914	0.657	1.2458	0.8468	5700	330

[a] Reference 8. [b] Reference 25.

Table III
Heats of Mixing to Infinite Dilution

system	t, °C	$\Delta H^M(\infty)$, J g⁻¹
PDMS-MEK	20	14.4
	35	14.3
	50	14.3
PDMS-MIBK	20	9.9
	35	9.0
PDMS-EBK	35	8.8
	50	8.7_8
PDMS-DIBK	35	6.1

Table IV
Exchange Parameters X_{12} and Q_{12}

s_2/s_1	t, °C	X_{12}, J cm⁻³	Q_{12}, J cm⁻³ deg⁻¹
	PDMS-MEK		
0.69	20	24.7	−0.0587
	35	24.6	−0.0596
	50	24.6	−0.0604
	PDMS-MIBK		
0.68	20	17.0	−0.0377
	35	15.5	−0.0423
	PDMS-EBK		
0.70	35	14.5	−0.0322
	50	14.4	−0.0331
	PDMS-DIBK		
0.75	35	9.4	−0.0212

of $\Delta H^M(\infty)$ decreases with increasing number of carbon atoms in the solvent molecule. This tendency is the same as that obtained by Patterson[28] for PDMS–alkyl ester systems.

According to Flory's theory,[5,6] the heat of mixing to infinite dilution is given by

$$\Delta H^M(\infty) = (v_{sp,2}^*/\tilde{v}_1)\{(1 + \alpha_1 T)X_{12}(s_2/s_1) + p_2^*[\tilde{v}_1/\tilde{v}_2 - 1 - (1 - T_1^*/T_2^*)\alpha_1 T]\} \quad (4)$$

where X_{12} is the exchange enthalpy parameter, v_{sp}^* is the specific characteristic volume, subscripts stand for components, and s_2/s_1 is the ratio of the surface area per segment for polymer to that for solvent. The method of determination of the ratio is described later. The third column of Table IV shows X_{12} values obtained from $\Delta H^M(\infty)$ (eq 4). For the MEK and EBK systems, the values of X_{12} are nearly independent of temperature in this temperature range. The enthalpy parameter X_{12} is useful for discussion of the explicit difference of the contact enthalpic interactions between the segments of different molecules. The value of X_{12} obtained for the DIBK system is the smallest, while that for the MEK system is the largest; i.e., the value of X_{12} decreases as the number of methyl or methylene groups in the solvent molecule increases. This may be due to the following effect: the contribution of the contact interaction between methyl or methylene groups in the solvent molecule and methyl groups in the polymer molecule to X_{12} increases with an increase of the number of methyl or methylene groups in the solvent molecule, and consequently the contribution of the contact interaction between the carbonyl group in the solvent molecule and the methyl group in the polymer molecule diminishes. A similar trend was found for PDMS–dialkyl ether systems by Morimoto,[26] although the values of X_{12} for these systems are smaller because the C–O–C bond in the dialkyl ether molecule is more similar to the Si–O–Si bond than to the C=O bond in the dialkyl ketone molecule. X_{12} found from these results reflects the exchange enthalpy well.

Osmotic pressures measured in the polymer concentration range of about 9–30 wt % for the four systems are shown with weight fractions w_2 and segment fractions φ_2 in Table V. The segment fraction is obtained from the weight fractions and characteristic specific volumes by

$$\varphi_2 = w_2 v_{sp,2}^*/(w_1 v_{sp,1}^* + w_2 v_{sp,2}^*) \quad (5)$$

Table V also shows interaction parameters χ determined from osmotic pressures π by

$$(\mu_1 - \mu_1^0)/RT = -\pi V_1^0/RT = \ln (1 - \varphi_2) + (1 - 1/r)\varphi_2 + \chi\varphi_2^2 \quad (6)$$

where $\mu_1 - \mu_1^0$ is the chemical potential of the solvent, V_1^0 is the molar volume of the solvent, R is the gas constant, and r is the ratio of the number of segments of the polymer molecule to that of the solvent molecule.

According to Flory's new theory,[5,6] χ is represented by

$$\chi = (p_1^* V_1^*/RT\varphi_2^2)\{3\tilde{T}_1 \ln [(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + (\tilde{v}_1^{-1} - \tilde{v}^{-1})\} + V_1^* X_{12}\theta_2^2/\tilde{v}RT\varphi_2^2 - V_1^* Q_{12}\theta_2^2/R\varphi_2^2 \quad (7)$$

where V_1^* is the characteristic molar volume of the solvent, θ_2 is the surface fraction given by

$$\theta_2 = s_2\varphi_2/(s_1\varphi_1 + s_2\varphi_2) \quad (8)$$

and Q_{12}, defined analogously to X_{12} and added only to χ,

Table V
Osmotic Pressures and Interaction Parameters

t, °C	w_2	φ_2	$10^4\pi$, J cm^{-3}	χ
		PDMS–MEK		
20	0.0956	0.0849	41.2	0.521
	0.1360	0.1213	55.9	0.539
	0.1963	0.1765	133.6	0.558
	0.2274	0.2052	156.1	0.572
	0.2704	0.2454	239.8	0.590
	0.3384	0.3097	498.6	0.620
35	0.1025	0.0912	63.2	0.517
	0.1767	0.1587	152.4	0.545
	0.2125	0.1917	237.5	0.557
	0.2704	0.2457	376.3	0.582
	0.3295	0.3016	766.4	0.604
50	0.0977	0.0869	81.0	0.506
	0.1693	0.1519	219.7	0.531
	0.2383	0.2157	441.4	0.558
	0.3381	0.3100	1127	0.598
		PDMS–MIBK		
20	0.1140	0.0982	105.4	0.494
	0.1428	0.1236	143.0	0.509
	0.1651	0.1434	193.4	0.516
	0.2235	0.1959	377.5	0.527
	0.2614	0.2305	509.0	0.550
35	0.1040	0.0899	103.6	0.484
	0.1412	0.1227	190.5	0.494
	0.1667	0.1454	259.5	0.504
	0.2023	0.1775	390.1	0.515
	0.2328	0.2052	532.8	0.525
	0.2769	0.2457	797.8	0.541
		PDMS-EBK		
35	0.0973	0.0848	88.6	0.482
	0.1581	0.1390	223.3	0.500
	0.2504	0.2231	619.2	0.528
	0.3303	0.2978	1100	0.566
50	0.0975	0.0851	114.3	0.470
	0.1462	0.1285	229.7	0.489
	0.2314	0.2059	609.4	0.514
	0.2922	0.2623	994.1	0.539
		PDMS–DIBK		
35	0.0999	0.0854	108.5	0.451
	0.1371	0.1180	165.5	0.478
	0.1594	0.1377	260.7	0.470
	0.2042	0.1777	433.2	0.484
	0.2237	0.1952	552.8	0.486
	0.2514	0.2203	705.9	0.496

represents the entropy change due to interactions between unlike segments. In the infinite dilution limit, we have

$$\lim_{\varphi_2\to 0} \chi = \chi_1 = (p_1{}^*V_1{}^*/\tilde{v}_1RT)(A^2\alpha_1T/2 + Y_{12}) - V_1{}^*Q_{12}/R(s_1/s_2)^2 \quad (9)$$

where

$$A = (1 - T_1{}^*/T_2{}^*)(p_2{}^*/p_1{}^*) - (s_2/s_1)X_{12}/p_1{}^* \quad (10)$$

and

$$Y_{12} = X_{12}(s_2/s_1)^2/p_1{}^* \quad (11)$$

To calculate the theoretical values of χ from eq 7 and 9, we need to evaluate three parameters: s_2/s_1, X_{12}, and Q_{12}. In addition, the equation-of-state parameters need to be evaluated. The surface ratio s_2/s_1 has been determined from molecular models in many cases, but this method led to poor reproduction of the trend of χ with composition for the PDMS systems. Sugamiya et al.[20] examined several methods for evaluating s_2/s_1, but they failed to find a method that could be used for all systems. Therefore, we adopt the values which reproduce the trend of χ with composition best; these are shown in Table IV. Then, we obtain the values of X_{12} in Table IV. The dashed curves in Figure 1 were calculated from eq 7 and 9 with X_{12} and s_2/s_1 so determined and with $Q_{12} = 0$. The solid curves were calculated by adding a Q_{12} which was chosen to match the experimental values of χ. The values of Q_{12} are shown in the last column of Table IV. For each system, there are large discrepancies between the solid curves and the dashed curves. The Q_{12} term contributes about 0.21–0.24 to χ at infinite dilution. The absolute value of Q_{12} for the PDMS–DIBK system is the smallest, and that for the PDMS–MEK system the largest; the absolute values are dependent on the length of the solvent molecule.

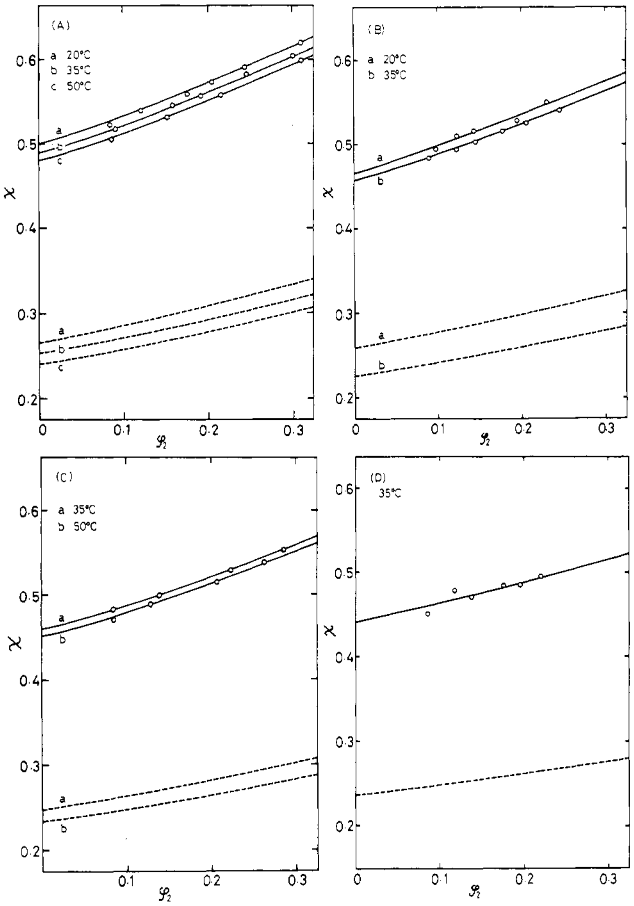

Figure 1. Interaction parameter χ vs. segment fraction φ_2 for PDMS systems: (A) PDMS–MEK system; (B) PDMS–MIBK system; (C) PDMS–EBK system; (D) PDMS–DIBK system. The circles are experimental values from osmotic pressures (eq 6). The dashed curves are calculated from eq 7 with $Q_{12} = 0$; solid curves are obtained by adding the Q_{12} term (see text).

Prausnitz et al.[22,23] attributed the source of Q_{12} to an overestimation of the combinatorial entropy given by the Flory–Huggins approximation; they proposed a combinatorial entropy of mixing containing a correction for molecular bulkiness. Their expression for the chemical potential is given by

$$(\mu_1 - \mu_1{}^0)/RT = \ln \varphi_1 + (1 - 1/r)\varphi_2 - \sum_{t=1}^{z}\alpha^{(t)}\{\ln [\varphi_1 + (q/r)^t\varphi_2] + [1 - (q/r)^t]\varphi_2\}/[1 - (q/r)^t]r + \chi\varphi_2{}^2 \quad (12)$$

where $\alpha^{(t)}$ is a parameter depending on the molecular size and shape, q is the ratio of the surface area for the polymer molecule to that for the solvent molecule, and z is the coordination number whose value is taken as 6. Here q/r is equivalent to s_2/s_1 in the Flory theory. The third term in eq 12 is the correction term for molecular bulkiness. Its contribution to the chemical potential becomes larger as q/r approaches zero. In the limit of $q/r \to 1$, eq 12 is identical with the Flory–Huggins equation, i.e., eq 6. In

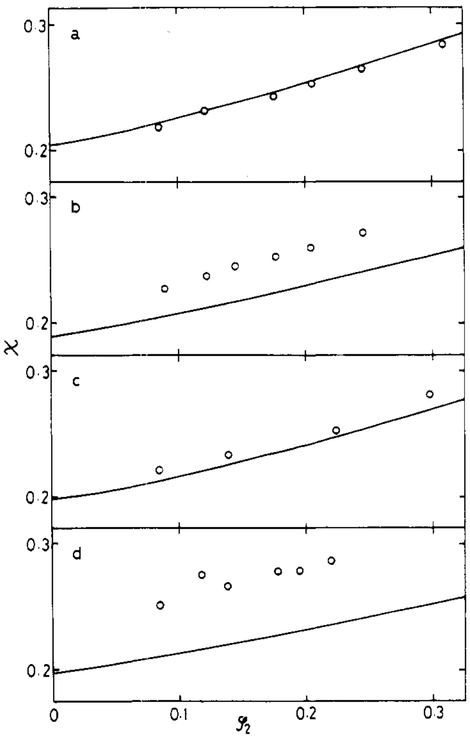

Figure 2. Interaction parameter χ vs. segment fraction φ_2: (a) PDMS-MEK system at 20 °C; (b) PDMS-MIBK system at 35 °C; (c) PDMS-EBK system at 35 °C; (d) PDMS-DIBK system at 35 °C. The circles are experimental values obtained from osmotic pressures (eq 12). The curves were calculated from eq 7 with $Q_{12} = 0$ (see text).

Figure 2, the values of χ obtained from osmotic pressures for the PDMS-MEK system at 20 °C and for the other systems at 35 °C by the use of eq 12 are compared with those calculated from eq 7 with $Q_{12} = 0$. The calculations were performed by using $s_2/s_1 = q/r = 0.52$, 0.57, 0.56, and 0.63 for the MEK, MIBK, EBK, and DIBK systems, respectively. Since these surface ratios were estimated from bond angles, bond lengths, and characteristic volumes, they were different from those shown in Table IV. Therefore, the values of X_{12} are also different. The experimental values of χ obtained from eq 12 are much smaller than those from eq 6 because of the smaller contribution of the combinatorial entropy to the chemical potential; they are closer to the theoretical values calculated according to eq 7.

Excess volumes measured for the four systems at 35 °C are shown in Figure 3 as the ratio of the volume change V^E on mixing to the sum V^0 of the volumes of the pure components. The absolute values of V^E/V^0 for these PDMS systems are much smaller than those for polyisobutylene systems. According to Flory's theory,[5,6] the excess volume is given by

$$V^E/V^0 = \tilde{v}^E/\tilde{v}^0 = \tilde{v}/\tilde{v}^0 - 1 \tag{13}$$

where

$$\tilde{v}^0 = \varphi_1\tilde{v}_1 + \varphi_2\tilde{v}_2 \tag{14}$$

The theoretical values at $\varphi_2 = 0.5$, calculated by using the values of X_{12} and s_2/s_1 in Table IV, are $V^E/V^0 = +0.11 \times 10^{-1}$, $+0.50 \times 10^{-2}$, $+0.47 \times 10^{-2}$, and $+0.27 \times 10^{-2}$ for the MEK, MIBK, EBK, and DIBK systems, respectively. The signs of the theoretical values are different from those obtained experimentally for all systems except the DIBK system. For each system, the difference between the calculated and observed values is large. Even for $X_{12} = 0$, which leads to poorer reproductions of experimental values of χ and $\Delta H^M(\infty)$, the signs of the theoretical excess volumes remain positive. Reproduction of the experimental values, shown by the solid curves in the figure, require negative values of X_{12}; $X_{12} = -45.4$, -18.9, -24.7, and -5.07 J cm^{-3} for the MEK, MIBK, EBK, and DIBK systems, respectively. Disagreement in the sign has been reported for other PDMS systems.[19]

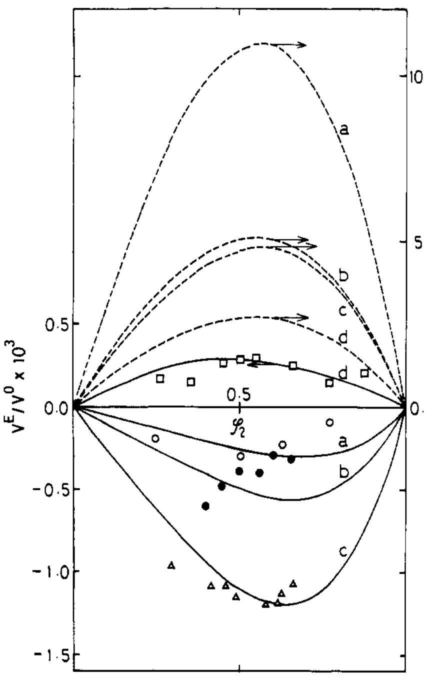

Figure 3. Experimental values of V^E/V^0 at 35 °C vs. segment fraction φ_2: (○) PDMS-MEK system; (●) PDMS-MIBK system; (△) PDMS-EBK system; (□) PDMS-DIBK system. The solid curves were calculated so as to match the experimental values; negative values of X_{12} were used as described in the text. The dashed curves were calculated by using X_{12}, obtained from $\Delta H^M(\infty)$.

The combinatorial entropy proposed by Prausnitz et al. appears to be successful for the present systems with small values of s_2/s_1. However, their expression underestimates the combinatorial entropy for polyisobutylene systems[29] because the values of s_2/s_1 for these systems are larger by only about 10% than those for the PDMS systems.[26] Therefore, their expression for the combinatorial entropy should be examined further by applying it to other systems, preferentially to PDMS systems with large values of s_2/s_1, where the value of the correction term is smaller. Therefore, in part 2 of this series, octamethylcyclotetrasiloxane (OMCTS) was chosen as solvent. In the PDMS-OMCTS system, it is expected that the value of the correction is small and, if the combinatorial entropy proposed by Prausnitz et al. is correct, recourse to Q_{12} in the Flory theory should be unnecessary. Also, investigations from other points of view are desirable since the discrepancy of the excess volume is not improved by corrections of the combinatorial entropy.[30]

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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

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

which is accurate to within ±0.5 × 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

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

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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