Dependence of interaction parameter on molecular weight and concentration for solutions of poly(dimethylsiloxane) in methylethylketone

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The polymer–solvent interaction parameter χ for solutions of poly(dimethylsiloxane) (PDMS) of different molecular weights (4600–220 000) in methylethylketone (MEK) at segment fractions of PDMS $\phi 2$ ranging from 0.3 to 0.7 was measured by means of the vapour pressure method at 30°C, (20°C higher than the θ temperature for the PDMS–MEK system). The χ values obtained experimentally were found to be almost independent of the molecular weight of PDMS. The observed X values were reproduced by applying Flory's new theory with evaluated values of three quantities: (1) the ratio of the surface area per segment for the polymer to that for the solvent s_2/s_1; (2) the enthalpy exchange parameter X_{12} and (3) the entropy exchange parameter Q_{12}.

Keywords Poly(dimethylsiloxane); interaction parameter; methylethylketone; molecular weight; equation of state; vapour pressure

INTRODUCTION

Poly(dimethylsiloxane) (PDMS) shows some distinctive features in chain construction; these include the long bond length of the Si–O bond, the small van der Waals radius of the O-atom and the large angle at the O-atom may conspire to reduce steric conflict but does not however, eliminate steric conflict for all chain conformations. The partition function for a solution of PDMS gives rise to an important effect on the residual free energy of mixing. The thermodynamic functions for the mixing of PDMS molecules with solvent molecules contain contributions from the exothermic orientation of the solvent molecules in cooperation with PDMS segments and from an endothermic effect arising from the solution of the polymer chains in the solvent[1]. Bianchi[2] has pointed out the effect of the conformational energy change in a polymer chain on the heat of mixing of a polymer with solvent, as shown with PDMS solutions[3]. These results have been interpreted with respect to the large radius of the PDMS segment, the existence of the oxygen atom in the PDMS backbone chain and chain flexibility[4].

The polymer–solvent interaction parameter χ for PDMS solutions has been determined by many workers[5–8]. This parameter contains two terms. The first term is due to the difference in the contact energy between segments of PDMS and the solvent molecules. The second is the difference in free volume termed 'structural effect', principally due to the difference in chain length or bulkiness between the chains[9].

PDMS has a remarkably high degree of thermal expansion, which is close to those of some solvents. Patterson and his coworkers[6] have investigated systems of PDMS and solvents by means of a vapour pressure method. Large negative values for $-\chi_s$ observed in these experiments suggested that the large negative non-combinatorial contribution is dominant for the entropy of dilution[6]. Patterson *et al.*[10] have elucidated the thermodynamic effect of the free volume change on mixing segments of PDMS with solvent molecules by the use of the corresponding state principle on non-polar polymer solution established by Prigogine[11]. Using this they explained the negative heats of mixing for systems of methylsiloxane oligomer and alternatively the positive heat of mixing for a system of the dimer and the polymer[12].

Flory *et al.*[13–16] have presented a new theory on the thermodynamics for polymer solutions on a similar basis and have expressed an equation representing the Gibb's free energy for the binary mixtures containing the polymer. This theory has enabled us to calculate the interaction parameters χ for polymer–solvent systems using measureable parameters such as the thermal expansivity α, the exchange interaction parameter X_{12} and so on. By assuming this theory, the dependence of χ on temperature and polymer concentration, and the excess volumes of mixtures of polymers with solvents were discussed by comparing the theoretically calculated values of χ with the experimental values[17–25].

Nakajima *et al.* proved that the thermodynamic quantities for polystyrene–MEK systems were appreciably well explained by Flory's new theory[26].

The contact energy term in the expression representing Flory's new theory is formulated by using the exchange interaction parameter $\bar{X}_{12}$. This parameter is experimentally determined through the heat of mixing to infinite dilution[17]. Determination of the heats of mixing for organosiloxane polymer systems have been presented in the literature. Patterson *et al.*[27] determined

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calorimetrically, the heats of mixing for dimethylsiloxane oligomers and polymer systems and showed that the heats of mixing for mixtures of PDMS in n-alkane except for n-pentane are positive, and alternatively, for mixtures of PDMS in the dimethylsiloxane dimer, negative. These phenomena have been verified on the basis of Prigogine's corresponding state theory. Hamada *et al.*[28] have published values for the heats of mixing to infinite dilution for mixtures of PDMS in aliphatic ketones. Morimoto[29] has determined calorimetrically, the heat of mixing at infinite dilution of PDMS solution in various solvents and obtained small values for the enthalpy exchange interaction parameter X_{12}.

The interaction parameter χ is principally independent of the molecular weight of polymer. However the chain molecule of PDMS is assumed to be flexible to the extent that it is feasible to take a variety of spatial configurations[30]. It has been ascertained[31] that the interaction sites for a PDMS molecule in solution are assumed to be in peripheral methyl groups and oxygen atoms of the chain, while the terminal methyl groups may exert the intermolecular forces differing from those of the mid-chain repeating units. The proportion of the former to the interaction energy probably decreases with the molecular weight of PDMS.

This paper is aimed at investigating the dependence of χ, for a solution of PDMS in MEK, on the molecular weight of PDMS. In addition, the experimental values of χ for solutions of PDMS with several molecular weights in MEK are discussed in comparison with the theoretical values evaluated on the basis of Flory's new theory.

EXPERIMENTAL

Materials

The PDMS samples used were commercial Toshiba silicone oils and silicone rubber. The bulk viscosities of the oils were ~100, ~500, ~2 000, ~10 000, and ~100 000 cSt at 25°C. The molecular structure of these samples is represented by:

$$(CH_3)_3Si\text{-}O\text{-}[(CH_3)_2Si\text{-}O]_n\text{-}Si(CH_3)_3.$$

With highly viscous samples the low-boiling constituents were removed by fractional precipitation from solutions in ethyl acetate by the addition of methyl alcohol as a precipitant, according to the procedure described in the literature[32]. The average molecular weight $\bar{M}$ was determined from the intrinsic viscosities in toluene using Barry's[33] relationship for the molecular weight for a PDMS homologous series. The numerical values of $\bar{M}$ obtained were 4600, 16 000, 40 000, 55 000, and 220 000.

Reagent grade MEK used as the solvent was purified by distillation. Solutions of PDMS in MEK were gravimetrically prepared. PDMS samples were dissolved in MEK and aged for a few days to make uniform solutions of known weight fractions of PDMS ranging from 0.3 to 0.7.

Measurement of the chemical potential

The chemical potentials of the solvent were determined by the lowering of the vapour pressure of the solvent on solutions of PDMS relative to that on the pure solvent, using differential manometers as reported in a previous paper[8]. The solutions were maintained at 30°C ± 0.001°C.

Measurement of χ

The values of χ were calculated from the following equation[8]:

$$\begin{aligned}\mu_1-\mu_1^0&=RT\ln a_1\\&=RT[\ln(1-\varphi_2)+(1-1/x)\varphi_2+\chi\varphi_2^2]\end{aligned}\qquad(1)$$

where $(\mu_1=\mu_1^0)$ is the difference in the chemical potentials between the solvent in the polymer solution and the pure solvent, a_1 is the activity of the solvent in the solution and was calculated from the ratio $\Delta P/P_0$ of the lowering of vapour pressure of solvent on the solution to that on the pure solvent. x is the ratio of the molar volumes of polymer to solvent. The segment fraction of PDMS φ_2 in the solution was calculated from the weight fraction w_2 on the assumption that no volume change occured on mixing and φ_2 was defined by:

$$\varphi_2=w_2v_{sp,2}^*/(w_1v_{sp,1}^*+w_2v_{sp,2}^*)\qquad(2)$$

where $v_{sp,1}^*$ and $v_{sp,2}^*$ are the characteristic specific volumes of the solvent and the polymer, respectively.

Experimental results are listed in *Table 1*, and *Figure 1* shows the plots of experimental values of χ against φ_2.

Equation of state parameter

The equation of state parameters for PDMS and MEK used here were available from Flory's data[14,16], as shown in *Table 2*. The parameters for MEK were obtained by interpolating data cited in the literature[34].

The densities, ρ_2, of the PDMS samples were measured with pycnometers in the temperature range 25°–35°C. The regression lines fitted to obtained results were expressed by

$$\rho_2=-8.859\times10^{-4}t+0.9828$$

for molecular weight of 4600; (3a)

Table 1 Measurements of χ for solutions of PDMS in MEK

Average molecular weight	ϕ_2	$\Delta P/P_0$	χ
4 600	0.370 0.504 0.695	0.0248 0.0579 0.1488	0.486 0.538 0.684
16 000	0.336 0.524 0.673	0.0196 0.0567 0.1219	0.474 0.583 0.699
40 000	0.402 0.491 0.715	0.0293 0.0449 0.1600	0.514 0.576 0.720
55 000	0.317 0.486 0.682	0.0170 0.0427 0.1291	0.470 0.577 0.702
61 000	0.350 0.525 0.725	0.0216 0.0582 0.1668	0.477 0.577 0.736
220 000	0.366 0.502 0.674	0.0261 0.0467 0.1229	0.471 0.583 0.694

$$\rho_2 = -8.796\times10^{-4}t + 0.9893$$
$$\text{for } 16\,000; \tag{3b}$$

$$\rho_2 = -8.780\times10^{-4}t + 0.9908$$
$$\text{for } 40\,000; \tag{3c}$$

$$\rho_2 = -8.777\times10^{-4}t + 0.9911$$
$$\text{for } 55\,000; \tag{3d}$$

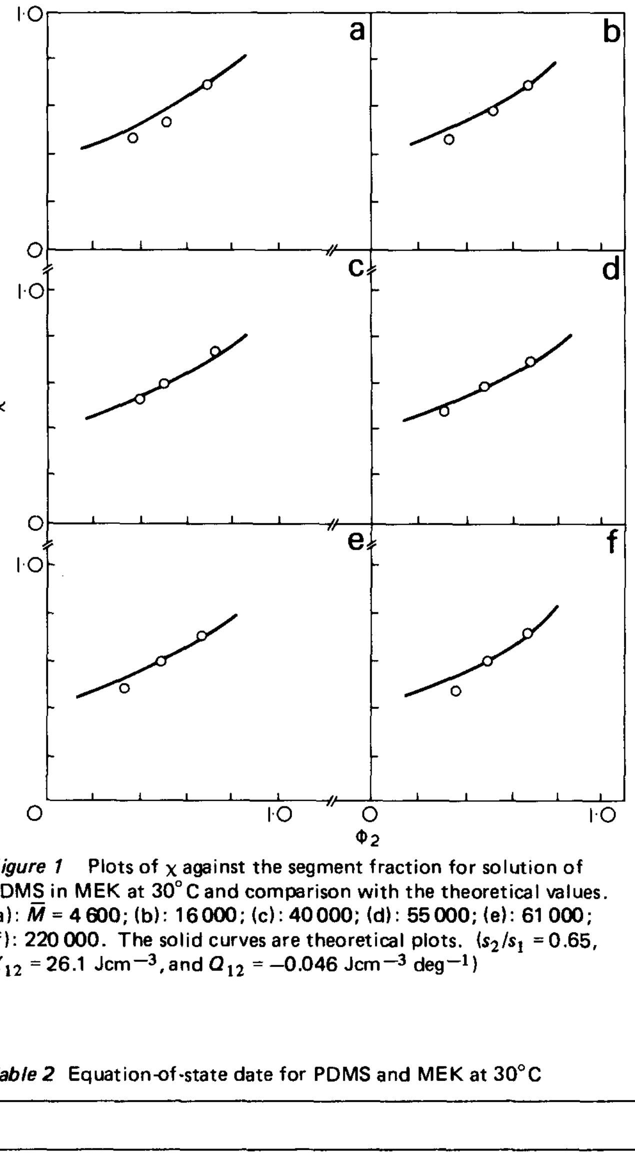

Figure 1 Plots of χ against the segment fraction for solution of PDMS in MEK at 30°C and comparison with the theoretical values. (a): $\bar{M}$ = 4 600; (b): 16 000; (c): 40 000; (d): 55 000; (e): 61 000; (f): 220 000. The solid curves are theoretical plots. (s_2/s_1 = 0.65, X_{12} = 26.1 Jcm^{-3}, and Q_{12} = −0.046 Jcm^{-3} deg^{-1})

$$\rho_2 = -8.777\times10^{-4}t + 0.9912$$
$$\text{for } 61\,000; \tag{3e}$$

and

$$\rho_2 = -8.772\times10^{-4}t + 0.9917$$
$$\text{for } 220\,000, \tag{3f}$$

where temperature t is measured in °C and ρ_2 in g cm^{-3}. The mean deviation of the values calculated according to these equations from the observed results is within ±0.00064 g cm^{-3}.

The thermal expansivities α_2 for each of the PDMS samples at 30°C was obtained by dividing the slope expressed by equation (3) by the values of density ρ_2 calculated by equation (3) at 30°C, respectively. A plot of α_2 against the reciprocal of the molecular weight of PDMS was found to be linear, expressed by

$$\alpha_2 = 0.8447(1/M) + 9.082\times10^{-4} \tag{4}$$

The characteristic pressure parameter p_2^* for PDMS has been found to be constant independent of the molecular weight of PDMS[35]. The reduced volumes $\tilde{v}_2$ of PDMS samples were calculated using the following equation

$$\tilde{v}_2^{1/3} = 1 + \frac{\alpha_2 T}{3(1+\alpha_2 T)} \tag{5}$$

The characteristic temperature T_2^* for the PDMS samples were calculated using the equation

$$\frac{T^*}{T} = \frac{\tilde{v}_2^{4/3}}{\tilde{v}_2^{1/3} - 1} \tag{6}$$

The specific core volume for PDMS $v_{sp,2}^*$ was calculated with the use of ρ_2 from the relation

$$v_{sp,2}^* = (1/\rho_2)\tilde{v}_2 \tag{7}$$

being used for calculation of φ_2 using equation (2).

The value of the reduced volume for solution of PDMS in MEK, $\tilde{v}$, was determined by using the equation

$$\frac{T^*}{T} = \frac{\tilde{v}^{4/3}}{\tilde{v}^{1/3} - 1} \tag{8}$$

Table 2 Equation-of-state date for PDMS and MEK at 30°C

			PDMS			
$\bar{M}$	ρ_2 (g cm^{-3})	$10^4\ \alpha_2$ (K^{-1})	$\tilde{v}_2$	$v_{sp,2}^*$ (cm^3 g^{-1})	T^* (K)	p_2^* (Jcm^{-3} K^{-1})
4 600	0.9562	9.265	1.2356	0.8464	5498.4	339
16 000	0.9629	9.135	1.2328	0.8424	5543.0	
40 000	0.9645	9.103	1.2321	0.8414	5554.0	
55 000	0.9648	9.097	1.2320	0.8413	5556.0	
61 000	0.9649	9.096	1.2320	0.8412	5556.6	
220 000	0.9654	9.086	1.2318	0.8409	5560.1	
			MEK[14,16]			
ρ_1 (g cm^{-3})	$10^3\ \alpha_1$ (K^{-1})	γ_1 (Jcm^{-3} K^{-1})	$\tilde{v}_1$	$v_{sp,1}^*$ (cm^3 g^{-1})	T_1^* (K)	p_1^* (Jcm^{-3} K^{-1})
0.7945	1.324	1.104	1.13145	0.9575	4571.7	578.0

Table 3 Theoretical values of χ for solutions of PDMS in MEK at 30°C

Average molecular weight	φ_2	Equation of state term	Contact interaction term	χ
4600	0.2	0.0000	0.4546	0.455
	0.4	0.0003	0.5342	0.535
	0.6	0.0012	0.5986	0.600
	0.8	0.0034	0.7746	0.778
16000	0.2	0.0003	0.4574	0.458
	0.4	0.0000	0.5344	0.534
	0.6	0.0004	0.6220	0.622
	0.8	0.0024	0.7099	0.712
40000	0.2	0.0003	0.4547	0.455
	0.4	0.0000	0.5345	0.535
	0.6	0.0005	0.6223	0.623
	0.8	0.0086	0.7756	0.784
55000	0.2	0.0091	0.4547	0.464
	0.4	0.0000	0.5357	0.536
	0.6	0.0005	0.6223	0.623
	0.8	0.0020	0.7756	0.778
61000	0.2	0.0001	0.4547	0.455
	0.4	0.0000	0.5357	0.536
	0.6	0.0005	0.6223	0.622
	0.8	0.0019	0.7758	0.776
220000	0.2	0.0001	0.4547	0.455
	0.4	0.0000	0.5357	0.536
	0.6	0.0005	0.6222	0.623
	0.8	0.0019	0.7838	0.786

in which T^* is the characteristic temperature for the solution, the numerical value of which was determined by substituting the values of the parameters p_1^*, p_2^*, T_1^*, T_2^*, and $\bar{X}_{12}$ as cited later, into the equation

$$T^* = \frac{\varphi_1 p_1^* + \varphi_2 p_2^* - \varphi_1 \varphi_2 \bar{X}_{12}}{\dfrac{\varphi_1 p_1^*}{T_1^*} + \dfrac{\varphi_2 p_2^*}{T_2^*}} \quad (9)$$

the values of $\tilde{v}$ obtained were then used to calculate the theoretical values of χ.

Calculation of theoretical value for χ

Theoretical value for χ for the solution of PDMS in MEK was obtained by applying Flory's new theory[14,16] according to the equation

$$\chi = (p_1^* v_1^* / RT\varphi_2^2)\{3T_1 \ln[\tilde{v}_1^{1/3} - 1)/\tilde{v}^{1/3} - I)] + (\tilde{v}_1^{-1} - \tilde{v}^{-1})\} - (v_1^* \theta_2^2 / \tilde{v}\varphi_2^2 RT)\bar{X}_{12} \quad (10)$$

where the site fraction θ_2 is given by the equation

$$\theta_2 = \frac{s_2}{s_1}\varphi_2 \bigg/ \left(\varphi_1 + \frac{s_2}{s_1}\varphi_2\right) \quad (11)$$

where s_2/s_1 is the ratio of the contact sites per segment for the polymer to that for the solvent, being determined as the value of χ calculated from equation (10) required to reproduce the experimentally observed value. The exchange interaction parameter $\bar{X}_{12}$ was estimated by the equation (13) presented by Flory *et al.*[18,30]

$$\bar{X}_{12} = X_{12} - \tilde{v}TQ_{12} \quad (12)$$

where X_{12} and Q_{12} have been defined as the enthalpy exchange parameter and the entropy exchange parameter, respectively. By simulating in equation (10), the value of s_2/s_1 used here was determined as 0.65, holding commonly for the molecular weights of PDMS from 4600 to 220000 used here.

The value of X_{12} for solutions of PDMS in MEK has been found to be 24.6 J cm^{-3} at 30°C from the heat of mixing ΔH_∞^M at infinite dilution by Shiomi and his coworkers[37] using the equation with $s_2/s_1 = 0.69$.

$$\Delta H_\infty^M = (v_{sp,2}^* / \tilde{v}_1)[(1 + \alpha_1 T)X_{12}(s_2/s_1) + p_2^*\{(v_1/v_2 - 1) - (1 - T_1^*/T_2^*)\alpha_1 T\}] \quad (13)$$

In this experiment the value of s_2/s_1 found to reproduce the best values of χ was 0.65. Recalculation of the X_{12} value by using $s_2/s_1 = 0.65$ gave 26.1 J cm^{-3}.

The value of Q_{12} was evaluated so as to give the value of χ, calculated by equation (10), which reproduced the experimentally obtained value of χ. The value of $Q_{12,i}$ for each individual solution used was calculated by using equation (10) with $X_{12} = 26.1$ J cm^{-3}, $s_2/s_1 = 0.65$ and by taking into consideration the value of χ obtained experimentally for the solution. The average value of $Q_{12,i}$ was -0.046 J cm^{-3} deg^{-1} and the standard deviation was 0.004 J cm^{-3} deg^{-1}.

Theoretical calculations for χ were performed by substituting 0.65, 26.1 J cm^{-3}, and -0.046 J cm^{-3} deg^{-1} for s_2/s_1, X_{12}, and Q_{12}, into equation (10), respectively. Results for these calculations are displayed in *Table 3*, in which the equation of state term and the contact interaction term designate the second term (in the bracket) of equation (10) and the last term in equation (10), respectively. The solid curves in *Figure 1* express the theoretical values of χ against φ_2.

RESULTS AND DISCUSSION

It has been clearly shown by preliminary experiment[38] that the temperature dependence of χ for the solution of PDMS in MEK is hardly revealed at around 30°C. Presupposing the above result, this experiment was carried out at a constant temperature, 30°C, selected close to the θ temperature, 25°C for the system. Also, the values of χ for the solutions of PDMS with molecular weights 4600–220000, in MEK were found to be slightly dependent on temperature within the range 25°–35°C at moderate concentration. Therefore, the aim of the experiment was to clarify the effect of the molecular weight of PDMS on the concentration dependence of χ at 30°C.

Figure 1 shows the observed values of χ at 30°C for the MEK solutions of PDMS with varying molecular weights. From the figure it is clear that the values of χ increase with increasing concentrations of PDMS in the range of φ_2 from 0.37 to 0.73. This fact agrees well with the results obtained by Chahal *et al.*[6]. To investigate the variation of χ with the molecular weight of PDMS, the values of χ at given values of φ_2 were read off from the curves connecting plots of χ against φ_2. The result is shown in *Figure 2*. It is ascertained in this figure that the χ value for the solution of PDMS in MEK is independent of the molecular weight of PDMS in the range of the molecular weights higher than 4600.

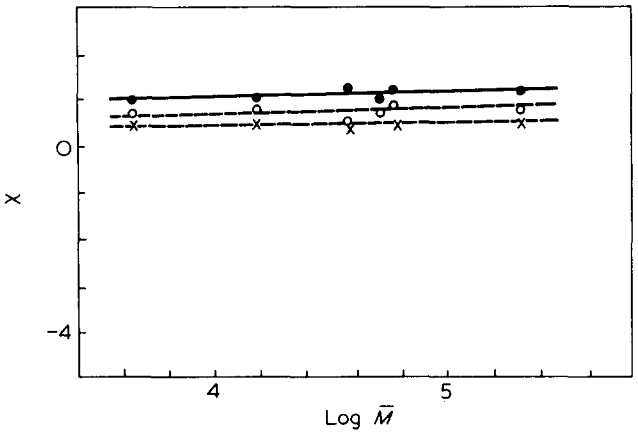

Figure 2 Molecular weight dependence of χ for solution of PDMS in MEK at 30°C. Solid line: $\phi_2 = 0.60$, dotted: 0.50, broken: 0.37

The results obtained were analysed on the assumption of Flory's new theory[14,16]. Theoretical values of χ for each of the solutions of PDMS of different molecular weights studied here are calculated using equation (10), and are shown in *Table 3*. The maximum deviation between the experimental and theoretical values of χ at the same concentration is *ca.* 9.7%, as shown in *Figure 1*. This result suggests that the experimental value of χ conforms to Flory's theory.

The ratio s_2/s_1 in the range studied here is a main factor to decide the concentration dependence of χ. The value of s_2/s_1 is required to be estimated exactly and, in general, the ratio s_2/s_1 has not been evaluated accurately since the molecular shape of PDMS in solution is not comparable with the crystallographically evaluated molecular dimension. The values of s_2/s_1 for the PDMS–MEK system have been reported by several authors. Hamada and his coworkers[31] reported a value of 0.72 which was expected to reproduce the concentration dependence of χ in the range of 0.1 to 0.33 weight fraction of PDMS. Morimoto[29] has demonstrated a method for evaluating the ratio s_2/s_1 and obtained a value of 0.44 for the PDMS–MEK systems, which is too small to reproduce the experimental value.

Furthermore, Lichtenthaler *et al.*[39] have taken into consideration the geometry of the ratio of surface contact sites per segment for the repeating unit of the polymer and the solvent molecule, for calculating the ratio s_2/s_1. However, the result, $s_2/s_1 = 0.578$, calculated by applying the theory, is too small to reproduce the experimental value of χ in this work.

Flory *et al.*[40] have presented an equation for evaluation of the ratio s_2/s_1

$$s_2/s_1 = (V_1^*/V_m^*)(s_m/s_1). \tag{14}$$

The surface area of the MEK molecule is estimated by the approximation of a cylinder with the characteristic volume $V_1^* = 69.04\ \text{cm}^3\ \text{g}^{-1}$ and a circular section radius of 2.8 Å and a length 7.3 Å. The PDMS molecule was assumed to be represented by a cylinder composed of n units, each having the characteristic volume V_m^*, circular section radius 3.37 Å and length 2.9 Å per unit. The result shows that s_2/s_1 is independent of the molecular weight of PDMS, as shown in *Table 4*. The average value of s_2/s_1 thus obtained was 0.70. This value is nearly in agreement with the value of $s_2/s_1 = 0.65$, simulated in this experiment, although the quantities used for calculating the molecular surface areas of PDMS and MEK remain uncertain.

Experimental values of the enthalpy exchange parameter X_{12} and the entropy exchange parameter Q_{12} for solutions of PDMS are presented in *Table 5*. This table shows that these parameters are not immediately dependent on the molecular shape and size or the kinds of groups of the solvent molecule comprising the components. This trend agrees with the findings for the solutions of aliphatic and aromatic components, respectively[16].

The reduced volume $\tilde{v}$ for a segment in solution is treated as functions of the characteristic temperature T_2^* and the thermal expansion coefficient α_2 for a polymer as shown in equations (4), (5), (7), and (8), the quantities of which are associated with the molecular weight of the polymer as shown in *Table 2*. However the variation of α_2 with the molecular weight of PDMS gives only a slight fluctuation in the reduced volume $\tilde{v}$ for a segment in solution with the change of the molecular weight of PDMS studied here.

The first two terms in the bracket in equation (10) indicate the equation of state term, depending on the reduced volume $\tilde{v}$ for a segment in solution. These terms are nearly equal to each other in absolute value but opposite in sign, for the systems studied here. Therefore, the equation of state terms for the systems studied here are negligible, as shown in *Table 3*.

Consequently, the variation of the interaction parameter χ with the molecular weight of PDMS does not seem to be appreciable as shown in *Figure 2*, in spite of the fact that the three parameters stated above vary with the molecular weight of PDMS.

It can be assumed that the interaction state of the terminal segment differs from that of the mid-chain segment, since the terminal group of PDMS is a methyl group in place of the silicon linkage and the mid-chain oxygen. Therefore, the contribution of terminal segment to the total interaction energy is conceivably dependent on the molecular weight. In this study, however, the effect of the terminal segment on χ was not considered.

Table 4 Characteristic volumes of MEK and PDMS at 30°C

MEK V_1^* (cm³ mol⁻¹)	PDMS M	V_2^* (cm³ mol⁻¹)	V_m^* (cm³ mol⁻¹)	s_2/s_1
69.04	4 600	3 893	62.74	0.697
	16 000	13 478	62.40	0.702
	40 000	33 656	62.33	0.703
	55 000	46 272	62.36	0.702
	61 000	51 315	62.35	0.702
	220 000	184 994	62.29	0.703

Table 5 Enthalpic exchange parameters X_{12} and entropic exchange parameters Q_{12} for solutions of PDMS

Solvent	X_{12} (Jcm⁻³)	Q_{12} (Jcm⁻³ deg⁻¹)	Ref.
Benzene	22.0	−0.0420	40
Cyclohexane	8.0	−0.039	
Chlorobenzene	11.0	−0.0640	
Ethylbutylketone	14.5	−0.0322	37
Methylethylketone	26.1	−0.046	This work

The intermolecular attractive fields of PDMS segments for the interaction with MEK molecules reside mainly in the peripheral methyl groups of PDMS, while it has been pointed out that the interactions between the methyl groups of PDMS and the O-atom of carbonyl groups in MEK are present[31]. The contributions of these effects to the interaction between PDMS segments and MEK molecules are presumed to be simultaneous. It may be suggested, therefore, that the values of X_{12}, Q_{12}, and s_2/s_1 obtained in this study represent an average for these two interaction modes, respectively.

CONCLUSION

The experimental values of χ for the moderately concentrated solutions of PDMS, of various molecular weights, in MEK were well explained on the basis of Flory's new theory. Three quantities s_2/s_1, X_{12}, and Q_{12} characterizing the system, were taken as constant, within the limits of experimental error, despite the molecular weight of PDMS varying in the range of 4600–220000. Values of χ for the system were independent of the molecular weight of PDMS over the range 4600 to 220000. The reason for this seems to be that α_2 for PDMS and $\tilde{v}$ for the solutions are almost constant in this range of molecular weights, and that the equation of state term for this system is negligibly small and therefore the value of χ is almost dominated only by the exchange energy term.

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