to characterize the intermolecular energy in liquids, only through the factor $\tilde{v}^2$. We take p^* to be a measure of the mean intermolecular energy per unit volume corrected for the density of packing in the liquid. Values of p^* correlate favorably with the chemical nature of the liquid (see Table III and ref 2). For polystyrene (PS) and ethylbenzene, they are virtually coincident. We observe in particular the low values of p^* for PDMS and for HMDS and their similarity. They are much smaller than for organic liquids in general; comparable values are found only for the fluorocarbons.[16] Thus, the intermolecular energies for the methylsiloxanes are extraordinarily low. Although the origins of this peculiarity are obscure, it obviously underlies many of the properties of polymers in this series, *e.g.*, their low viscosities and the low temperature coefficients of their viscosities.

On the other hand, the indicated low value of the intermolecular energy density is not reflected in the interactions between PDMS and various solvents. Cohesive energy densities (ced) estimated from "solubility" or swelling measurements[15] indicate a value on the order of that found for aliphatic hydrocarbons and certainly greater than the ced for fluorocarbons, in which PDMS is insoluble. The large discrepancy between ced and p_i (and hence p^*) for PDMS has been pointed out by Allen, Gee, and coworkers.[8,15]

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(16) A. Abe and P. J. Flory, *J. Amer. Chem. Soc.*, **88**, 2887 (1966).

Thermodynamics of Solutions of Poly(dimethylsiloxane) in Benzene, Cyclohexane, and Chlorobenzene

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ABSTRACT: Excess volumes have been measured at 25° for mixtures of poly(dimethylsiloxane) (PDMS) of high molecular weight with each of three solvents: benzene, cyclohexane, and chlorobenzene. Chemical potentials have been determined for solutions in the first two of these solvents by high-pressure osmometry and by vapor sorption. These results, in conjunction with osmotic measurements by Kuwahara, *et al.*, in chlorobenzene at 20 and 60°, and the heats of mixing determined by Delmas, *et al.*, for each of these systems permit a comprehensive analysis of the thermodynamic properties of the PDMS mixtures. They are characterized by entropies of dilution and excess volumes that are abnormally low compared with theoretical calculations.

A number of investigations have been reported on the thermodynamic properties of mixtures of poly(dimethylsiloxane) (PDMS) and its oligomers with various organic solvents. Most of these studies have dealt primarily with the heats of mixing. Delmas, Patterson, and Bhattacharyya[1] determined heats of mixing ΔH_M^∞ to infinite dilution for PDMS in various solvents including benzene, cyclohexane, and chlorobenzene, and in mixtures of these solvents. Patterson, Bhattarcharyya, and Picker[2] carried out similar calorimetric measurements on binary mixtures of several oligomers of PDMS and of the dimer with PDMS itself. Morimoto[3] summarized and discussed calorimetric results for mixtures of PDMS with a large number of organic solvents. Dreifus and Patterson[4] reported heats of mixing for PDMS with *n*-alkanes and with several of its oligomers. Kuwahara, Okazawa, and Kaneko[5] have reported osmotic pressures of PDMS solutions in cyclohexane, toluene, and chlorobenzene at concentrations ranging from volume fractions of 0.07 to 0.25, *i.e.*, well above the usual dilute range. Malcolm and Koh[6] investigated the thermodynamic properties of chloroform and carbon tetrachloride solutions of a low molecular weight PDMS, covering the entire concentration range, and measured excess volumes as well. Recently Summers, Tewari, and Schreiber[7] have determined the activities of a number of hydrocarbons in PDMS in the "Henry's law" range of high concentration of polymer by use of gas–liquid chromatography.

Interpretation of the results of these investigations has been hampered by lack of reliable equation-of-state data for the polymer, a deficiency remedied by the results offered in the preceding paper.[8] Most of the investigations cited have been restricted in scope, being concerned with only one of the properties of the mixture, *i.e.*, with its excess enthalpy, or the chemical potential. Only the work of Malcolm and Koh[6] included determinations of both of these properties and the excess volume as well. The latter property is an important one with respect to the interpretation of interactions in mixtures.[9,10]

In this paper we present experimental measurements of excess volumes for mixtures of PDMS with three solvents: benzene, cyclohexane, and chlorobenzene. Chemical potentials in the former two solvents are reported, these being determined by osmometry and vapor sorption; the work of Kuwahara, *et al.*,[5] on chlorobenzene solutions obviated os-

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(1) G. Delmas, D. Patterson, and S. N. Bhattacharyya, *J. Phys. Chem.*, **68**, 1468 (1964).

(2) D. Patterson, S. N. Bhattacharyya, and P. Picker, *Trans. Faraday Soc.*, **64**, 648 (1968).

(3) S. Morimoto, *Makromol. Chem.*, **133**, 197 (1970).

(4) D. W. Dreifus and D. Patterson, *Trans. Faraday Soc.*, **66**, 631 (1970).

(5) N. Kuwahara, T. Okazawa, and M. Kaneko, *J. Polym. Sci., Part C*, No. **23**, 543 (1968).

(6) G. N. Malcolm and S. P. Koh, *Discuss. Faraday Soc.*, **49**, 164 (1970), and private communication.

(7) W. R. Summers, Y. B. Tewari, and H. P. Schreiber, *Macromolecules*, **5**, 12 (1972).

(8) H. Shih and P. J. Flory, *ibid.*, **5**, 758 (1972).

(9) A. Abe and P. J. Flory, *J. Amer. Chem. Soc.*, **87**, 1838 (1965).

(10) P. J. Flory, *Discuss. Faraday Soc.*, **49**, 7 (1970).

TABLE I
EQUATION-OF-STATE DATA AND CHARACTERISTIC PARAMETERS FOR SOLVENTS AT SELECTED TEMPERATURES

	Benzene[a] 25°	Cyclohexane[a] 25°	Chlorobenzene 20°	Chlorobenzene 60°
ρ, g cm^{-3}	0.8738[b]	0.7739[d]	1.1053	1.0621
$\alpha \times 10^3$, deg^{-1}	1.223[b]	1.217[d]	0.957	1.035
γ, J cm^{-3} deg^{-1}	1.263[c]	1.067[c]	1.341	1.092
$\tilde{v}$	1.2917	1.2906	1.2356	1.2789
$\tilde{T}$	0.06332	0.06316	0.05510	0.06156
v^*, cm^{-3} g^{-1}	0.8860	1.0012	0.7323	0.7362
T^*, K	4709	4721	5320	5412
p^*, J cm^{-3}	628	530	600	595

[a] See ref 9. [b] S. E. Wood and J. P. Brusie, *J. Amer. Chem. Soc.*, **65**, 1891 (1943). [c] G. A. Holder and E. Whalley, *Trans. Faraday Soc.*, **58**, 2095 (1962). [d] S. E. Wood and J. A. Gray, *J. Amer. Chem. Soc.*, **74**, 3729 (1952).

motic and vapor sorption studies on this system. It has been necessary for the interpretation of the results, however, to determine the equation-of-state parameters for chlorobenzene. The parameters for the other two solvents are available from literature sources.

Experimental Section

The PDMS used in all experiments reported below had been freed of low molecular weight constituents as described in the preceding paper.[8] Its molecular weight was *ca.* 10^5. Benzene, cyclohexane, and chlorobenzene were of spectroquality or analytical reagent grade. The density, thermal expansivity, and thermal pressure coefficient of chlorobenzene were measured by methods fully described elsewhere.[11,12]

Osmotic pressures were measured over the intermediate range of composition using the high-pressure osmometer described previously.[13,14] Schleicher and Schuell 08 membranes were used. They were conditioned by successively transferring them from a 3:1 mixture of water and 2-propanol, to 1:3 water–2-propanol, to 1:3 solvent (benzene or cyclohexane)–2-propanol, to 1:1 solvent–2-propanol, to 3:1 solvent–2-propanol, and finally to the pure solvent. The membrane was stored in each mixture for a period of two hours.

Solvent activities at higher concentrations were determined by the vapor sorption method.[14,15] The weight of solvent absorbed was determined from the extension of a calibrated quartz helix. Pressures were measured with a Bourdon gauge made of fused quartz.[14]

Excess volumes for mixtures of PDMS with each of the solvents were measured directly by observation of the change in volume upon dissolution. Polymer (3–5 g) and solvent were placed in separate bulbs of a glass cell of the design described previously,[14,16] the passage between the two bulbs being blocked initially by mercury. The mercury was displaced by tilting the cell. Thorough mixing was achieved by intermittently rotating the cell manually during a period of 2 hr. Owing to the comparatively low viscosity of PDMS, magnetic stirring was not required as with other, less mobile polymers.[16] The difference between the positions of the liquid miniscus in a calibrated capillary before and after mixing at 25.00° yielded the volume change.

Equation-of-State Data and Characteristic Parameters

The required data comprising densities ρ, thermal expansivities $\alpha = v^{-1}(\partial V/\partial T)_p$, and thermal pressure coefficients $\gamma = (\partial p/\partial T)_V$ over suitable ranges of temperature are available for benzene and cyclohexane from literature sources as detailed below. Those for chlorobenzene were determined by well-established methods described elsewhere.[11,17] Our results for this liquid, extending over the temperature range 20–110°, are represented by

$$\rho = 1.1262_0 - 1.034_9 \times 10^{-3}t - 6.0_6 \times 10^{-7}t^2 + 7._8 \times 10^{-10}t^3 \text{ in g cm}^{-3} \quad (1)$$

in grams per cubic centimeter, and by

$$\gamma = 14.79 - 7.12 \times 10^{-2}t + 1.12 \times 10^{-4}t^2 \quad (2)$$

in bars per degree, where t is the Celsius temperature. The standard deviations between calculated and observed values are 5×10^{-5} g cm^{-3} for ρ and 0.03 bar deg^{-1} for γ. From eq 1 we obtain

$$\alpha\ (\text{deg}^{-1}) = 0.918_9 \times 10^{-3} + 1.92 \times 10^{-6}t + 1.9 \times 10^{-10}t^2 \quad (3)$$

Values of the foregoing quantities for chlorobenzene at the temperatures at which osmotic measurements were carried out by Kuwahara, Okazawa, and Kaneko[5] are given in the last two columns of Table I. Those for benzene and cyclohexane at 25°, the temperature chosen for the thermodynamic measurements that follow, are given in preceding columns of the table. The reduced volumes $\tilde{v}$ and reduced temperatures $\tilde{T}$, and the characteristic parameters v^*, T^*, and p^* given in the following rows of the table have been calculated from ρ, α, and γ through use of the relations

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

$$v^* = (\rho \tilde{v})^{-1} \quad (5)$$

$$\tilde{T} = T/T^* = (\tilde{v}^{1/3} - 1)\tilde{v}^{-4/3} \quad (6)$$

$$p^* = \gamma T \tilde{v}^2 \quad (7)$$

Values of these quantities for PDMS are given in the preceding paper.

The System Benzene–PDMS. Osmotic pressures π were measured at 25° over the composition range 0.139–0.235, expressed in weight fraction w_2 of polymer. The lower limit of this range is high enough to assure copious overlapping of polymer domains as required to obviate consideration of nonuniformity in the distribution of polymer segments. The usual thermodynamic formulas should therefore be applicable in principle.

Vapor sorption measurements of the solvent activity a_1 were carried out from w_2 = 0.50–0.90, also as 25°. Values of the reduced residual chemical potential[10] χ were calculated for each concentration at which either π or a_1 was measured through use of the familiar relation

$$\chi = (\mu_1 - \mu_1^0)/RT\varphi_2^2 - [\ln(1 - \varphi_2) + (1 - 1/r)\varphi_2]/\varphi_2^2 \quad (8)$$

where $\mu_1 - \mu_1^0$ is the difference between the chemical potentials for the solvent in the solution and in the pure solvent (*i.e.*,

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(11) R. A. Orwoll and P. J. Flory, *J. Amer. Chem. Soc.*, **89**, 6814 (1967).

(12) H. Höcker, G. J. Blake, and P. J. Flory, *Trans. Faraday Soc.*, **67**, 2251 (1971).

(13) P. J. Flory and H. Daoust, *J. Polym. Sci.*, **25**, 429 (1957).

(14) B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, **64**, 2035 (1968).

(15) L. Mandelkern and F. A. Long, *J. Polym. Sci.*, **6**, 457 (1951); S. Prager and F. A. Long, *J. Amer. Chem. Soc.*, **73**, 4072 (1951).

(16) P. J. Flory and H. Höcker, *Trans. Faraday Soc.*, **67**, 2258 (1971).

(17) G. Allen, D. Sims, and G. J. Wilson, *Polymer*, **2**, 375 (1961).

$\mu_1 - \mu_1^0 = -\pi V_1$, or $\mu_1 - \mu_1^0 = RT \ln a_1$); φ_2 is the segment fraction of polymer defined by

$$\varphi_2 = w_2 v_2^* / (w_1 v_1^* + w_2 v_2^*) \qquad (9)$$

the solvent and solute being identified by subscripts 1 and 2, and r is the ratio V_2^*/V_1^* of the characteristic molar volumes of the two components. For the polymer (mol wt $\approx 10^5$) in benzene $r \approx 1.2 \times 10^3$. Results are shown by the points in Figure 1. Included also is the result, indicated by a triangular point on the right-hand ordinate axis, obtained by Summers and coworkers[7] using the gas–liquid chromatographic method.

The curve in Figure 1 was calculated from the theoretical relation[10,18]

$$\chi = (p_1^* V_1^* / RT\varphi_2^2)\{3\tilde{T}_1 \ln [(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + (\tilde{v}_1^{-1} - \tilde{v}^{-1})\} + (V_1^* \bar{X}_{12}/\tilde{v}RT)(\theta_2/\varphi_2)^2 \qquad (10)$$

where V_1^* is the characteristic molar volume of the solvent (*i.e.*, the product of its molecular weight and v_1^* given in Table I), $\bar{X}_{12}$ is the exchange interaction parameter, and θ_2 is the surface fraction of the solute given by

$$\theta_2 = \varphi_2/[\varphi_1(s_1/s_2) + \varphi_2] \qquad (11)$$

Here s_1/s_2 is the ratio of surface areas per unit characteristic volume for solvent and solute. Estimation of this ratio for benzene–PDMS in the approximation that the solvent may be represented by a sphere and the solute by a cylinder[14,16] gives $s_1/s_2 = 1.67$. Estimation from the sum of the surface areas of constituent groups, the tabulations of group surface areas given by Bondi[19] being used for this purpose, yields $s_1/s_2 = 1.14$. The former is doubtless too large, the latter too small. The intermediate value $s_1/s_2 = 1.32$ best reproduces the trend of χ with composition. The curve in Figure 1 was calculated with s_1/s_2 so assigned and with $\bar{X}_{12} = 38$ J cm^{-3}. Summers and coworkers[7] obtained the comparable result $\bar{X}_{12} = 35$ J cm^{-3} from their gas–liquid chromatographic measurements yielding the triangular point at $\varphi_2 = 1$ in Figure 1. The overbar has been affixed to $\bar{X}_{12}$ above to signify that it may include entropic as well as energetic contributions to the change in interaction associated with changes of neighboring species. In terms of the notation adopted in preceding papers[14,16,20]

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

where X_{12} represents the enthalpy exclusively and Q_{12} is the corresponding parameter for the exchange entropy; $\tilde{v}$ denotes the reduced volume of the mixture.

The heat of mixing ΔH_M^∞ of PDMS to infinite dilution in benzene has been measured calorimetrically at 25° by Delmas, Patterson, and Bhattacharyya,[1] who obtained $\Delta H_M^\infty = 14.2$ J g^{-1}, and also by Morimoto,[3] who obtained a somewhat lower value, 11 J g^{-1}. According to the theory leading to eq 10[14]

$$\Delta H_M^\infty = (v_2^*/\tilde{v}_1)[X_{12}(s_1/s_2)^{-1} + p_2^*(\tilde{v}_1/\tilde{v}_2 - 1) - \alpha_1 T p_1^* A] \qquad (13)$$

where

$$A = (1 - T_1^*/T_2^*)(p_2^*/p_1^*) - (X_{12}/p_1^*)(s_1/s_2)^{-1} \qquad (14)$$

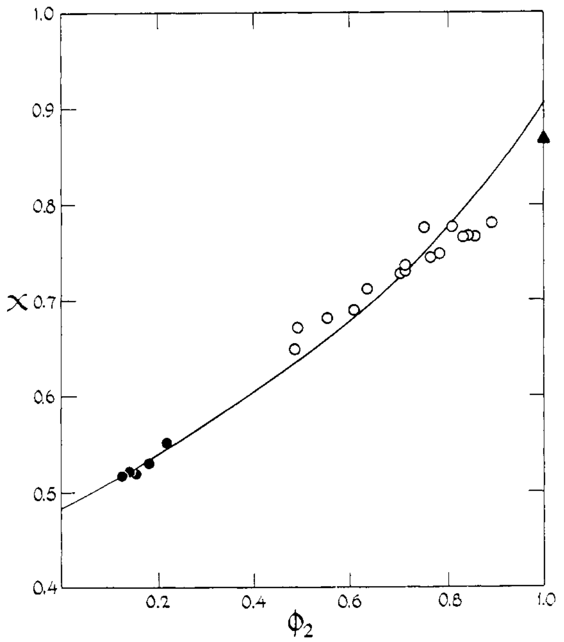

Figure 1. The reduced residual chemical potential χ plotted against segment fraction for the system C_6H_6–PDMS at 25°. Osmometric results are represented by filled circles, vapor pressure results by open circles. The result obtained by Summers, *et al.*,[7] by application of the method of gas–liquid chromatography is shown by a triangular point. The curve has been calculated according to theory using parameters given in the text.

If, on the presumption that the exchange entropy Q_{12} may be neglected, we let $X_{12} = \bar{X}_{12} = 38$ J cm^{-3}, the value adopted above in order to match the chemical potential, then from eq 13 we obtain $\Delta H_M^\infty = 22.1$ J g^{-1}, which is substantially greater than found by experiment. The result of Delmas, *et al.*, is reproduced by taking $X_{12} = 22.0$ J cm^{-3}. (The reduced equation of state is altered by reassignment of X_{12}. Hence, it does not suffice to reevaluate the first term in eq 13; the equation-of-state contributions represented by the last two terms in eq 13 are altered as well.)

The disparity between $\bar{X}_{12}$ derived from the chemical potential and X_{12} obtained from the enthalpy of mixing suggests at once that the former includes a substantial entropy contribution. Agreement with both the chemical potentials and the enthalpy of mixing is achieved by taking $X_{12} = 22.0$ J cm^{-3} and $Q_{12} = -0.0420$ J cm^{-3} deg^{-1}, or $-\tilde{v}TQ_{12} \approx 16.2$ J cm^{-3}, the value of the latter quantity depending somewhat on composition through the change of $\tilde{v}$ with φ_2, which for the present system is comparatively small. The source of Q_{12} could alternatively be attributed, in whole or in part, to overestimation of the combinatory entropy by the usual expressions. In any event, the magnitude of Q_{12} for the C_6H_6–PDMS system is unusually large. It contributes 0.20 to the value of χ at infinite dilution (see below), *i.e.*, to

$$\chi_1 \equiv \lim_{\varphi_2 \to 0} \chi = 0.481$$

(In the formulation of the theory the exchange entropy has been taken,[14,16,20] somewhat arbitrarily, to be independent of the volume. Hence, the reduced volume $\tilde{v}$ depends on X_{12} but not on Q_{12}. It follows that equation-of-state contributions to the thermodynamic properties are altered by separation of the entropic exchange interaction from the value of $\bar{X}_{12}$ calculated as above from the chemical potential. For the C_6H_6–PDMS system, the equation-of-state contributions to the free energy, and the chemical potential,

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(18) P. J. Flory, *J. Amer. Chem. Soc.*, **87**, 1833 (1965).
(19) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
(20) R. A. Orwoll and P. J. Flory, *J. Amer. Chem. Soc.*, **89**, 6822 (1967).

TABLE II
EXCESS VOLUMES FOR C_6H_6–PDMS MIXTURES AT 25°

φ_2	$(V^E/V^0) \times 10^2$
0.339	−0.038
0.396	−0.077
0.406	−0.068
0.454	−0.067
0.539	−0.056

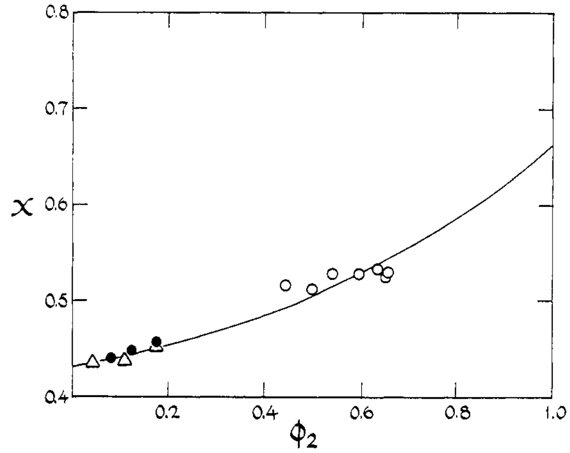

Figure 2. Values of χ plotted against composition for the system C_6H_{12}–PDMS. Triangles are representative osmotic results of Kuwahara, Okazawa, and Kaneko[5] at 20°. Results of the present investigation determined at 25° are shown by filled and open circles for osmotic and vapor sorption measurements, respectively. The curve has been calculated from theory as explained in the text.

are unusually small; hence the curve calculated for X_{12} = 22.0 J cm^{-3} and Q_{12} = −0.042 J cm^{-3} deg^{-1} differs little from the one calculated with X_{12} = 38 J cm^{-3} and Q_{12} = 0. Equation-of-state contributions to the enthalpy and to the entropy treated separately are appreciable, however; see below.)

Excess volumes measured at 25° are reported in Table II as the ratios of the volume change V^E on mixing to the sum V^0 of the volumes of the pure components. The changes are very small, but consistently negative. The theoretical value calculated for φ_2 = 0.50 using the parameters adopted above (s_1/s_2 = 1.32 and X_{12} = 22.0 J cm^{-3}) is 0.97 × 10^{-2}. The discrepancy, exceeding 1% of the total volume, is extraordinarily large.[9,10] It cannot be resolved by any reasonable adjustment of the parameters. For example, even for X_{12} = 0 the calculated value of $\tilde{v}^E/\tilde{v}^0 = V^E/V^0$ at φ_2 = 0.50 is 0.80 × 10^{-2}; if, in the other extreme, we let X_{12} = 38 J cm^{-3}, then $\tilde{v}^E/\tilde{v}^0$ = 1.21 × 10^{-2} according to theory.

The System Cyclohexane–PDMS. Results of our osmotic and vapor sorption measurements, treated in the manner described above for the C_6H_6–PDMS system, are represented in Figure 2 by filled and open circles, respectively. Kuwahara, *et al.*,[5] have carried out precise measurements of osmotic pressures for this system over the range from φ_2 = 0.025 to 0.176. Our results are in good agreement with theirs after recalculation of their χ values using segment fractions instead of volume fractions in eq 8 in order to achieve consistency with the present procedure. (Over the specified concentration range, values of χ calculated on the basis of volume fractions are lower by 0.008–0.012 than those calculated using segment fractions. Our choice of segment fraction in eq 8 rather than volume fraction is essentially arbitrary.) Representative results from their paper are shown by triangles in Figure 2.

TABLE III
EXCESS VOLUMES FOR CYCLOHEXANE–PDMS MIXTURES AT 25°

φ_2	$(V^E/V^0) \times 10^2$
0.394	0.057
0.419	0.052
0.508	0.053
0.513	0.065
0.636	0.055

TABLE IV
EXCESS VOLUMES FOR CHLOROBENZENE–PDMS MIXTURES AT 25°

φ_2	$(V^E/V^0) \times 10^2$
0.361	−0.41
0.432	−0.47
0.530	−0.50
0.629	−0.51

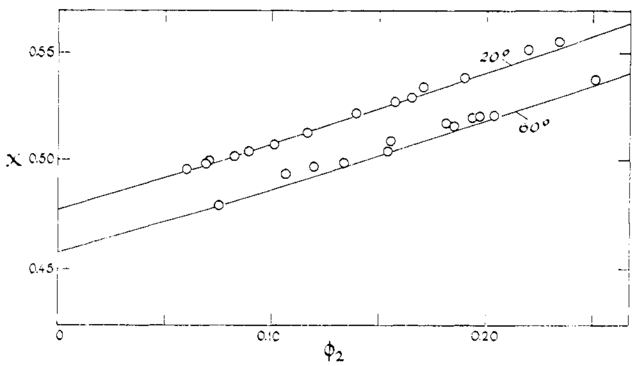

Figure 3. Results of Kuwahara, *et al.*,[5] for the system C_6H_5Cl–PDMS at 20 and 60°. The curves have been calculated from theory; see text.

The curve in Figure 2 has been calculated according to eq 10 with s_1/s_2 = 1.2, $\bar{X}_{12}$ = 23.0 J cm^{-1}, and Q_{12} = 0. The ratio s_1/s_2 = 1.2, chosen in order to reproduce the moderate increase of χ with φ_2, is much smaller than the value, 1.57, estimated in the "sphere-cylinder" approximation.

The integral heat of mixing ΔH_M^∞ to infinite dilution calculated according to eq 13 by taking $X_{12} = \bar{X}_{12}$ = 23.0 J cm^{-3} is 16.4 J g^{-1}, compared with 5.2 J g^{-1} found by Delmas, *et al.*,[1] from calorimetric measurements. Reproduction of their result requires X_{12} = 8.0 J cm^{-3}. Reconciliation of the calculations with both the chemical potentials and the enthalpy of mixing requires Q_{12} = −0.039 J cm^{-3} deg^{-1} to be used in conjunction with X_{12} = 8.0 J cm^{-3}. According to calculations carried out on this basis, the Q_{12} term makes a contribution of 0.275 to χ_1 = 0.429, the limiting value of χ at infinite dilution. Thus, the entropy deficit attributable to exchange interactions is very large, as for the preceding system.

Measured excess volumes are listed in Table III. They are consistently positive but very small. According to theory, with s_1/s_2 = 1.2 and X_{12} = 8.0 J cm^{-3}, V^E/V^0 = 0.71 × 10^{-2} at φ_2 = 0.5, which is considerably greater than the value observed.

The System Chlorobenzene–PDMS. Kuwahara, Okazawa, and Kaneko[5] have measured osmotic pressures of solutions of PDMS in chlorobenzene at 20 and at 60° over the range φ_2 = 0.07–0.25. Their results are shown in Figure 3. (Recalculation of values of χ using segment fractions instead of

TABLE V

RESUMÉ OF INTERACTION PARAMETERS AND REDUCED RESIDUAL PARTIAL MOLAR QUANTITIES

Solvent (temp, °C)	X_{12}, J cm^{-3}	$-\tilde{v}_1 T Q_{12}$, J cm^{-3} deg^{-1}	χ_1	$\chi_{H;1}$	$\chi_{H;1}$ exchange	$\chi_{S;1}$	$\chi_{S;1}$ exchange
C_6H_6 (25)	22.5	17.5	0.481	0.365	0.273	0.116	0.201
C_6H_{12} (25)	8.0	15	0.429	0.134	0.146	0.295	0.275
C_6H_5Cl (20)	11.0	23.2	0.477	0.197	0.154	0.280	0.323
C_6H_5Cl (60)	11.0	27.3	0.458	0.176			

volume fractions is unnecessary for this system owing to the fact that the difference between the reduced volumes $\tilde{v}_1$ and $\tilde{v}_2$ for solvent and solute is small.) The curves shown in the figure have been calculated from eq 10 using parameters as follows: $s_1/s_2 = 1.4$, $X_{12} = 11.0$ J cm^{-3}, and $Q_{12} = -0.0640$ J cm^{-3} deg^{-1}. The apportionment of the quantity $X_{12} - \tilde{v}TQ_{12}$ ($= X_{12} - \tilde{v}_1 TQ_{12} = 34.2$ at infinite dilution at 20°) between the enthalpic and entropic contributions was dictated by the change of χ with temperature as found by Kuwahawa, *et al.*; see Figure 3. In the limit of infinite dilution $\chi_1 = 0.477$ at 20° and 0.458 at 60° according to the calculated curves in Figure 3. These values of χ_1 are slightly greater (by 0.002 and 0.003, respectively) than those obtained by Kuwahara, *et al.*, by linear extrapolation.

The enthalpy of mixing ΔH_M^{∞} to infinite dilution calculated according to eq 13 through use of the parameters quoted above is 6.80 J cm^{-3}, in good agreement with the calorimetric result, 7.53 J cm^{-3}, of Delmas, *et al.*[1]

Excess volumes measured for this system are recorded in Table IV. Calculations carried out using the parameters above yield $V^E/V^0 = 0.25 \times 10^{-2}$ at $\varphi_2 = 0.50$ for a temperature of 25°. The observed results are much lower, the discrepancy being of about the same magnitude as found for the other two systems.

Discussion

Results of the analysis of observed heats of solution and chemical potentials for the three systems are summarized in Table V. Exchange interaction parameters are given in the second and third columns. The entropy parameter Q_{12} is represented by its contribution $-\tilde{v}_1 TQ_{12}$ to the total exchange interaction parameter denoted above by $\bar{X}_{12}$, this being the sum of enthalpic and entropic parts as specified in eq 12. Thus expressed, the magnitudes of the two contributions may be compared directly. Since the quantities appearing in the third column contain the reduced volume of the solvent, in a strict sense they apply only to the infinitely dilute solution. The reduced volumes $\tilde{v}$ for these systems do not depart greatly from the values of $\tilde{v}_1$ for the pure solvents; hence the restriction is not important.

Values of the reduced residual quantities appearing in succeeding columns of Table V refer to infinite dilution, as is denoted by the subscript 1. The choice has been dictated by convenience. It does not detract from the significance of comparisons of relative magnitudes of the various contributions to χ at any concentration inasmuch as the changes of the various quantities with concentration are similar within each of these systems. The reduced residual chemical potential χ_1 and the reduced residual partial molar enthalpy $\chi_{H;1}$ have been calculated from the following relationships obtained from the more general expressions by taking them to the limit $\varphi_2 = 0$[14, 18]

$$\chi_1 = (p_1{}^*V_1{}^*/RT\tilde{v}_1)[\bar{X}_{12}/p_1{}^*(s_1/s_2)^2 + (1/2)A^2\alpha_1 T] \quad (15)$$

$$\chi_{H;1} = (p_1{}^*V_1{}^*/RT\tilde{v}_1)(1 + \alpha_1 T)[X_{12}/p_1{}^*(s_1/s_2)^2 - (2/3)(A\alpha_1 T)^2] \quad (16)$$

where A is defined by eq 14. The reduced residual partial molar entropy at $\varphi_2 = 0$ is given by

$$\chi_{S;1} = \chi_1 - \chi_{H;1} \quad (17)$$

Exchange contributions to $\chi_{H;1}$ and $\chi_{S;1}$ are

$$\chi_{H;1}(\text{exch}) = V_1{}^*X_{12}/RT\tilde{v}_1(s_1/s_2)^2 \quad (18)$$

and

$$\chi_{S;1}(\text{exch}) = -V_1{}^*Q_{12}/R(s_1/s_2)^2 \quad (19)$$

Values of χ_1 thus obtained and recorded in Table V virtually represent experimental quantities, since the combined exchange parameter $\bar{X}_{12}$ has been so chosen as to reproduce χ_1 obtained by extrapolation of experimental measurements to infinite dilution.

The reduced residual partial molar enthalpies in the fifth column of Table V are subject to minor errors arising in consequence of inaccuracies of the theory as manifested in small changes of the characteristic parameters p^* and T^* (and hence in v^* as well; see ref 9 and 21) with temperature. In the derivation of eq 16 (*e.g.*, by differentiation of eq 15 with respect to temperature) these parameters are treated as constants. Thus, for the chlorobenzene system the calculated mean value of $\chi_{H;1}$ between 20 and 60° is 0.186, which is to be compared with the experimental result 0.156 obtained from the relation $\chi_{H;1} = -T(\partial\chi_1/\partial T)$ using the observed values of χ_1 at the two temperatures.

The contact exchange contributions to $\chi_{H;1}$ and $\chi_{S;1}$ account for the greater parts of these quantities. Equation-of-state contributions may be obtained by subtraction. It will be seen that these are of opposite sign in $\chi_{H;1}$ and $\chi_{S;1}$. Being of similar magnitude, their combined contribution to χ_1 is very small for these systems, in contrast to other polymer solutions that have been investigated.[10, 14, 16, 20, 22, 23]

The values of X_{12} increase in the order of the intermolecular energies of the solvents as represented by their p^*'s (see Table I). This order is consistent with the fact that p^* for PDMS is smaller than that for any of the solvents. Comparable values of X_{12} for benzene and chlorobenzene might have been expected on this basis. Possibly the permanent dipole moment of chlorobenzene enables it to interact favorably with the polar skeleton of the PDMS chain.

The most striking feature shared by all of the systems is the large value of $\chi_{S;1}$, which, as noted above, arises principally from the term in Q_{12}, equation-of-state contributions being small. As we have pointed out previously,[10, 14, 20] a negative value of Q_{12} (contributing positively to χ) may reflect over-

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estimation of the reduced partial molar combinatory entropy as incorporated in eq 8. However, so large an over-estimation, amounting roughly to half of the combinatory quantity whose value is $-{}^1/_2$ at $\varphi_2 = 0$, seems altogether implausible. Comparably large "entropy deficits" were found by Booth and Devoy[23] for benzene–polyoxyethylene and for benzene–polyoxypropylene. They attributed them to formation of weak charge-transfer complexes of benzene with the ether oxygens of the polymer chains. A corresponding explanation would be unfounded for the present systems.

Equally striking are the excess volumes which are consistently lower then predictions from theory by *ca.* 0.70×10^{-2}–1.0×10^{-2}, expressed as fractions of the total volume. Malcolm and Koh[6] likewise find excess volumes for the systems $CHCl_3$–PDMS and CCl_4–PDMS which are lower than values calculated similarly from theory, the discrepancies being of comparable magnitude to those found here. The benzene–poly(oxyethylene) system investigated by Booth and Devoy[23] does not share this discrepancy, good agreement having been found between observed and calculated excess volumes. For nonpolar solutions in general, the theory has been particularly successful in accounting for observed excess volumes. Solutions of PDMS in organic solvents appear to be exceptional in this regard.

One may plausibly assume the two discrepancies between experiment and theory, one in the entropy and the other in the excess volume, to be related. Peculiarities in the intermolecular force field may conceivably be responsible for both of them. Alternatively, an explanation may be found in the irregularity of the form of the PDMS chain, having pendant CH_3 groups spaced by comparatively long Si–O and Si–C bonds. Possibly the irregularity of the cross section of the chain obstructs efficient packing of the polymer chains in bulk. Effects of this nature should be ameliorated by molecules of the solvents here considered, which more easily fit into the irregularities. Such an accommodation of solvent molecules would entail a decrease of entropy as well as of volume.

Irrespective of the validity of the explanations suggested, it is to be hoped that more concrete generalizations will emerge from detailed investigations of a greater range of systems, with particular attention to the parameters p^* and T^* for the pure components and the exchange parameters X_{12} and Q_{12} for their mixtures.

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Dielectric Dispersion in Dilute Solutions of Poly(*p*-fluorostyrene), Poly(*m*-fluorostyrene), and Poly(*p*-chlorostyrene)[1]

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ABSTRACT: Dielectric loss tangents in dilute benzene solution at 25° have been measured from 10 to 150 MHz for three series of unfractionated halostyrene polymers, covering wide ranges of molecular weight. At sufficiently high molecular weights, the frequency of maximum loss is independent of molecular weight, but for molecular weights below about 2×10^4 it becomes gradually higher as the chain length decreases. This behavior can be quantitatively explained by the intrusion of overall rotatory diffusion as a mode of dipole relaxation competitive with local segmental motions. The slightly higher relaxation rate of poly(*m*-fluorostyrene) as compared to the para isomer is probably due to phenyl-group reorientation about the C_1–C_4 axis.

Polar groups in the repeat units of a polymer chain may conveniently be classified[2] into three types: (A) parallel to chain direction, (B) rigidly attached to chain backbone but perpendicular to chain direction, (C) on a flexible side chain. From a comparison between the experimental results[2,3] and the theoretical treatments,[4,5] it may be concluded that dielectric relaxation due to type A dipoles is well understood and that the existence of such a polar group in the repeat unit is a sufficient condition for a low-frequency dispersion with a molecular weight dependent relaxation time of the order of magnitude $\tau \cong M[\eta]\eta_0/RT$, where M is the molecular weight of the polymer, $[\eta]$ is the intrinsic viscosity of the polymer, η_0 is the viscosity of the solvent, R is the gas constant, and T is the absolute temperature.

Type B dipole moments, rigidly attached perpendicular to the direction of the chain contour, present a different and harder problem. For flexible chains, the vector sum of a sequence of such dipoles does not correlate with the end-to-end vector, so that the relevant modes of chain diffusion are usually short-range or local modes which cannot be meaningfully described by bead-and-spring models[4,5] except in a somewhat fictitious sense. Theoretically,[5,6] a true short-range mechanism within a flexible long chain must lead to a mean relaxation time independent of chain length, contrary to older predictions.[7-9] Experimentally it is in-

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