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Thermodynamics of Poly(methylphenylsiloxane)–Alkane Systems by Gas–Liquid Chromatography

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ABSTRACT: The specific retention volumes are reported of several alkane solutes on five poly(methylphenylsiloxane) (PMPS) stationary phases with different methyl/phenyl proportions at temperatures within 30–95 °C. The amounts of polymers in the columns employed have been determined by elemental analysis of the column packings. The methyl/phenyl proportions in the siloxane polymers have been obtained by NMR spectrometry. The activity coefficients and interaction parameters of the solutes at infinite dilution in the PMPS samples have been calculated from the specific retention volumes. From the activity coefficients and interaction parameters, the partial molar excess enthalpies of the solutes ($\Delta\bar{H}_1^{E\infty}$) and the polymer solubility parameters (δ_2) have been obtained. The effects of temperature and polymer composition on the values of $\Delta\bar{H}_1^{E\infty}$ and δ_2 are discussed.

Introduction

At present, the applications of gas chromatography to polymer solution studies concentrate mostly on thermodynamics of polymer blends. However, the revival of interest in supercritical fluid chromatography (SFC) during the past 10 years has restored the need for thermodynamic data on the individual (i.e., pure) polymers used as stationary phases in capillary SFC. For example, the polymer solubility parameters may be useful in simple models of the effect of polymer swelling by supercritical fluids on solute retention in capillary SFC.[1] The solubility parameters can be calculated[2] from the Flory-type interaction parameters, which in turn may be obtained by gas chromatography.

The most popular stationary phases for capillary SFC are siloxanes. Although there is a wealth of gas chromatographic studies of poly(dimethylsiloxane) (PDMS) solution thermodynamics,[3–15] little attention has been given to other siloxane polymers.[10,15,16] This paper presents the results of a gas chromatographic study of the interaction between several alkane solutes and several poly(methylphenylsiloxane) (PMPS) polymers with different methyl/phenyl proportions. Specific retention volumes, mass-fraction-based activity coefficients, and partial molar excess enthalpies of the solutes at infinite dilution in the PMPS samples are reported and compared to the respective characteristics of the alkane–PDMS[12] and alkane–poly[methyl(trifluoropropyl)siloxane] (PMTFPS)[16] systems. The effects of temperature and polymer composition on the excess enthalpies and polymer solubility parameters are discussed.

Experimental Section

Gas Chromatographic Measurements. The samples of PMPS were gas chromatographic stationary phases obtained from various suppliers under the commercial names SE 52, DC 550, OV 11, OV 17, and OV 25. They were used without further treatment to prepare the column packings. The solutes were reagent grade *n*-pentane, *n*-hexane, *n*-octane, *n*-nonane, and cyclohexane (Fluka AG, Buchs, Switzerland). The apparatus and procedures have been described previously.[12,16]

Elemental Analysis of the Column Packings. The uncertainty in the composition of the column packing is known[17,18] to be a major source of experimental error in the determination of specific retention volumes. Conventional gravimetric methods to determine the amount of polymer in the column packing are obviously unsuitable for siloxanes.[5,12,16] In this study, elemental analysis of the column packings has been employed. The method consists in a catalytic combustion of the sample in oxygen followed by gas chromatographic separation and quantitation of the carbon dioxide formed. A CHN-1 elemental analyzer (Laboratory equipments, Prague, Czechoslovakia) equipped with a Porapak Q separation column and a thermal conductivity detector has been used. The column temperature was 90 °C, the temperature of the combustion chamber was 1000 °C, and the carrier gas was helium. The instrument was calibrated with high-purity calcium carbonate. The sample sizes were 40–50 mg for the column packings and the bare solid support (0.40–0.63 mm Inerton AW HMDS, Lachema, Brno, Czechoslovakia) and 1–3 mg for the bulk siloxane polymers. Unlike our previous paper on the alkane–PMTFPS systems,[16] a single column was employed for each polymer in the present study. The mass fractions of polymers in the column packings were 0.062, 0.067, 0.076, 0.097, and 0.057 for SE 52, DC 550, OV 11, OV 17, and OV 25, respectively. The mass fractions obtained by elemental analysis were compared with the theoretical values calculated from the masses of the polymer and the support taken to prepare the packings; the differences between the corresponding values did not exceed 2.5% of the respective experimental mass fraction. In the case of OV-11, no bulk polymer was left for elemental analysis so that the theoretical result had to be used in the calculation of specific retention volumes.

NMR Measurements. The methyl/phenyl proportions in the individual polymers have been calculated from the areas of the respective multiplets in ^{1}H and ^{13}C FT NMR spectra of the polymer solutions (~20–30% v/v) in chloroform-*d*. The measurements were carried out with a Tesla BS 567 NMR spectrometer (Tesla, Brno, Czechoslovakia). The ^{1}H NMR spectra were recorded at a frequency of 100 MHz from four pulses per spectrum. The ^{13}C NMR spectra were generated at a frequency of 25.14 MHz from at least 1000 pulses per spectrum. With the

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Table I
Fractions of Phenyl in the Polymer Samples

polym	x_{Ph} ^{1}H NMR	 ^{13}C NMR	 mean
SE 52	0.058	0.057	0.058
DC 550	0.25	0.26	0.25
OV 11	0.31	0.31	0.31
OV 17	0.43	0.44	0.44
OV 25	0.70	0.73	0.72

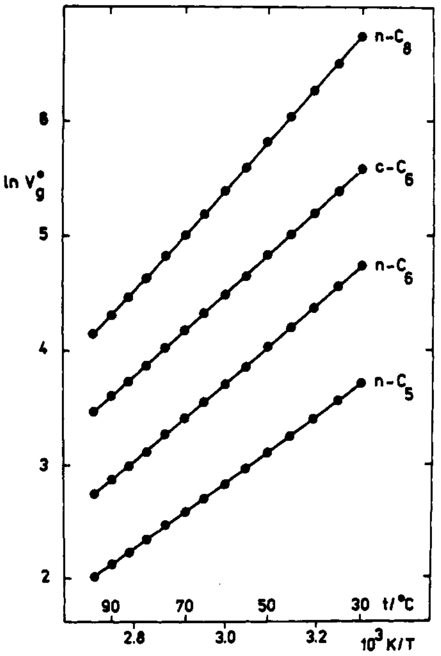

Figure 1. Temperature dependences of the specific retention volumes for the alkane–PMPS (OV 11) systems.

^{13}C NMR spectra, chromium(III) acetylacetonate was employed as a relaxation agent. In either case, the peak areas were obtained both electronicaly and manually (by a cut-and-weigh technique). In Table I, the resultant fractions, x_{Ph}, of the phenyl substituent in the polymer samples are listed. The overall uncertainty of these data may be estimated to be ±4%.

Data Reduction. The calculations of the mass-fraction-based activity coefficients, Ω_1^∞, and of the partial molar excess enthalpies, $\Delta\bar{H}_1^{E\infty}$, of the solutes from the specific retention volumes, V°_g, have been described in detail previously.[12,16] If the molar volume of the polymer is much larger than that of the solute, the infinite-dilution limit of the Flory–Huggins interaction parameter, χ^∞, is related to Ω_1^∞ by an approximate relation:[19]

$$\chi^\infty = \ln \Omega_1^\infty - \ln (v_1/v_2) - 1 \tag{1}$$

where v_1 and v_2 are the specific volumes of the solute and the polymer, respectively, at the given temperature. In this study, the specific volumes of the solutes were calculated from the Spencer–Adler correlation[20] for n-nonane and from the Campbell–Thodos correlation[21] for the other solutes. The specific volumes of the polymers have been assumed to vary linearly with x_{Ph} at a constant temperature. At 25 °C, v_2 = 1.0312 cm^3 g^{-1} for x_{Ph} = 0 (=PDMS),[22] and v_2 = 0.8787 cm^3 g^{-1} for x_{Ph} = 0.5.[23] For all the polymer samples, the thermal expansion coefficient has been assumed to be 9 × 10^{-4} K^{-1}.[22,24] The polymer solubility parameters have been obtained from[2]

$$\delta_1^2 - RT\chi^\infty/V^\circ_{1L} = 2\delta_1\delta_2 - \delta_2^2 - RT\beta/V^\circ_{1L} \tag{2}$$

where R is the gas constant, T is the thermodynamic temperature, V°_{1L} is the molar volume of the pure liquid solute, β is a dimensionless parameter related to the combinatorial entropy, and δ_1 and δ_2 are the solubility parameters of the solute and the polymer, respectively. The value of δ_2 may be estimated from the slope of a straight line obtained by plotting the left-hand side of eq 2 against δ_1.[2] The procedure used to calculate δ_1 as a function of temperature has been described previously.[14]

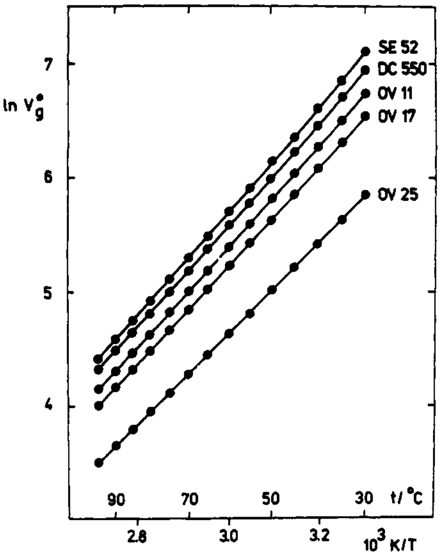

Figure 2. Temperature dependences of the specific retention volumes for the n-octane–PMPS systems.

Table II
Coefficients of the Equation ln $V^\circ_g = d \ln T + e/T + f$

solute/polym		SE 52	DC 550	OV 11	OV 17	OV 25
n-pentane	d	3.61	4.44	2.62	4.57	
	e	4280	4440	3810	4380	
	f	-30.63	-36.09	-23.84	-37.03	
n-hexane	d	4.71	5.43	3.47	3.48	-2.83
	e	5160	5300	4610	4530	2040
	f	-38.83	-43.55	-30.26	-30.25	13.35
cyclohexane	d	4.77	4.71	3.79	3.74	-3.04
	e	5310	5250	4930	4850	2290
	f	-39.02	-38.52	-32.34	-31.88	14.85
n-octane	d	6.84	6.25	5.34	5.52	3.73
	e	6920	6630	6270	6230	5300
	f	-54.77	-50.63	-44.43	-45.52	-32.95
n-nonane	d					4.72
	e					6130
	f					-40.39

Results and Discussion

Specific Retention Volumes. Figure 1 shows the plot of ln V°_g against 1000/T for the OV 11 polymer. The appearance of the respective plots for the other polymers is similar. Figure 2 shows the temperature courses of the specific retention volumes for n-octane with all the polymers studied. At a constant temperature, V°_g of n-octane decreases with increasing proportion of phenyl in the polymer, as expected. The same also applies to the other solutes employed. The experimental values of V°_g may be fitted by the relation

$$\ln V^\circ_g = d \ln T + e/T + f \tag{3}$$

The resultant values of the constants d, e, and f are listed in Table II (the units of V°_g are cm^3 g^{-1}). The differences between the experimental and calculated values of ln V°_g are on the order of 10^{-3}. The largest differences have been observed for the lowest retentions, i.e., for n-hexane and cyclohexane on OV 25. The respective constants of eq 3 differ markedly from those corresponding to the other solute–polymer pairs (cf. Table II). The specific retention volumes of the alkane solutes on the PMPS samples range between the corresponding values for PDMS and PMTFPS polymers. For example, at a given temperature, the specific retention volume of n-octane on PDMS[12] is by

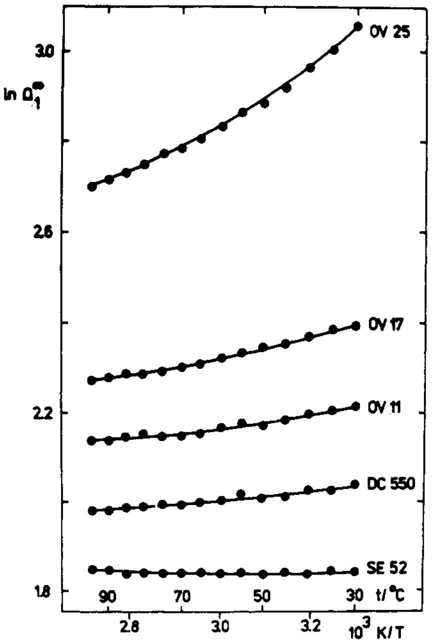

Figure 3. Temperature dependences of the activity coefficients for the n-hexane–PMPS systems.

Table III
Coefficients of the Equation $\ln \Omega_1^\infty = d \ln T + e/T + f$

solute/polym		SE 52	DC 550	OV 11	OV 17	OV 25
n-pentane	d	2.05	1.23	3.04	1.09	
	e	627	468	1100	526	
	f	−11.93	−6.47	−18.73	−5.54	
n-hexane	d	1.40	0.68	2.64	2.63	8.94
	e	458	320	1010	1090	3580
	f	−7.65	−2.93	−16.22	−16.23	−59.83
cyclohexane	d	0.95	1.01	1.93	1.98	8.76
	e	355	419	742	820	3380
	f	−4.95	−5.45	−11.63	−12.09	−58.82
n-octane	d	1.06	1.64	2.55	2.37	4.16
	e	430	722	1080	1120	2050
	f	−5.59	−9.73	−15.92	−14.83	−27.42
n-nonane	d					4.74
	e					2320
	f					−31.54

about 5% larger than that on SE 52, and the specific retention volume of n-octane on PMTFPS[16] is commensurate with that on OV 25.

Activity Coefficients and Interaction Parameters. Figure 3 shows the temperature dependences of the infinite-dilution mass-fraction-based activity coefficients of n-hexane in the PMPS samples. It is apparent from Figure 3 that the activity coefficients increase with increasing proportion of phenyl in the polymer. The temperature courses of $\ln \Omega_1^\infty$ may be fitted by an equation analogous to eq 3. The resultant constants d, e, and f are given in Table III.

The PMPS–alkane interaction parameters (eq 1) decrease with increasing temperature and increase with increasing proportion of phenyl in the polymer.

Partial Molar Excess Enthalpies. Table IV shows the values of $\Delta\bar{H}_1^{E\infty}$ for the solutes in PMPS at 60 °C. For a given solute, the excess enthalpies increase with increasing proportion of phenyl in the polymer (cf. the slopes of curves in Figure 3). With the n-alkane solutes, the values of $\Delta\bar{H}_1^{E\infty}$ increase with increasing carbon number of the solute. With SE 52, containing only ~6% of phenyl (cf. Table I), the values of $\Delta\bar{H}_1^{E\infty}$ are close to those observed in the alkane–PDMS systems.[12] The rather large values of $\Delta\bar{H}_1^{E\infty}$ for OV 25 are still lower than the corresponding data in the alkane–PMTFPS systems.[16] The method used here to obtain $\Delta\bar{H}_1^{E\infty}$ is known to be extremely sensitive to errors in the temperature derivative of $\ln \Omega_1^\infty$.[25] However, the trend in $\Delta\bar{H}_1^{E\infty}$ for a given solute with the PMPS, PDMS,[12] and PMTFPS[16] polymers is representative because the same routine has been followed in all cases.

Table IV
Infinite-Dilution Partial Molar Excess Enthalpies $\Delta\bar{H}_1^{E\infty}$ (J mol^{-1}) of the Solutes in PMPS at 60 °C

solute/polym	SE 52	DC 550	OV 11	OV 17	OV 25
n-pentane	−470	490	680	1350	
n-hexane	−64	770	1090	1800	4900
cyclohexane	320	690	840	1340	3850
n-octane	650	1460	1880	2720	5490
n-nonane					6130

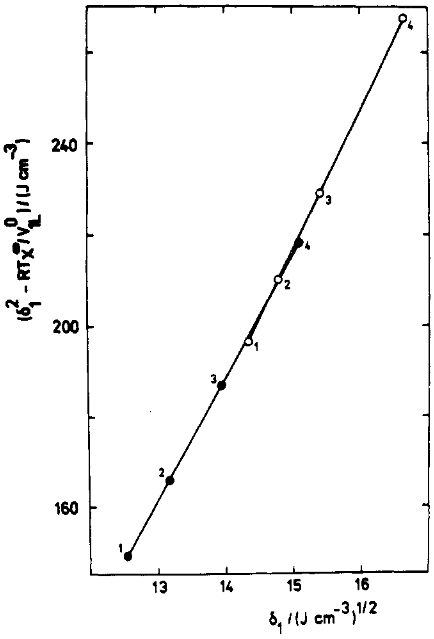

Figure 4. Determination of the solubility parameter of PMPS (SE 52) at 30 °C (○) and 90 °C (●): 1, n-pentane; 2, n-hexane; 3, n-octane; 4, cyclohexane.

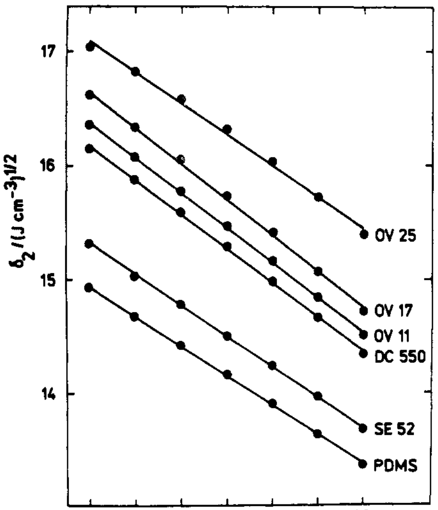

Figure 5. Temperature dependences of the polymer solubility parameters.

Solubility Parameters. The polymer solubility parameters, δ_2, have been calculated at temperatures from 30 to 90 °C in 10 °C steps. The data fits according to eq 2 are linear in all cases; two sample plots are shown in

Table V
Coefficients of the Equation $\delta_2 = a + bt$

polym	a, (J cm^{-3})$^{1/2}$	b, (J cm^{-3})$^{1/2}$ K^{-1}
PDMS	15.73	–0.0262
SE 52	16.15	–0.0273
DC 550	17.08	–0.0300
OV 11	17.30	–0.0307
OV 17	17.60	–0.0315
OV 25	17.92	–0.0276

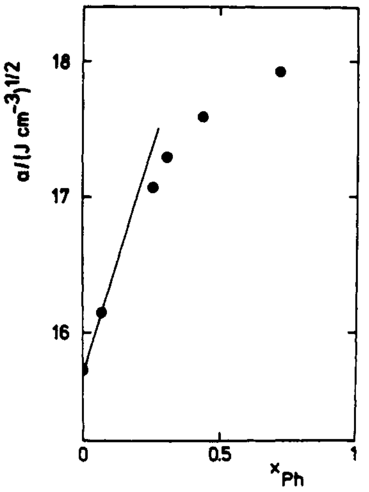

Figure 6. Constant a of eq 4 as a function of polymer composition.

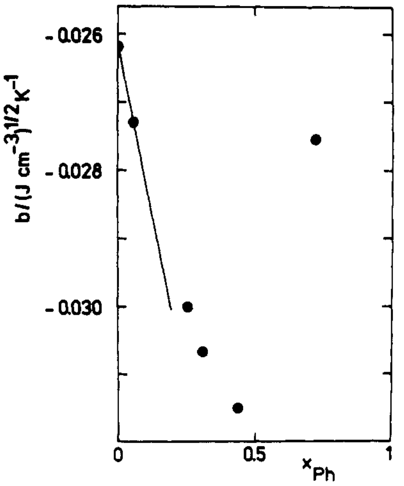

Figure 7. Constant b of eq 4 as a function of polymer composition.

Figure 4. The resultant δ_2 values are plotted against temperature in Figure 5 together with the data for PDMS.[14] The results may be fitted by an empirical linear relation:

$$\delta_2 = a + bt \qquad (4)$$

where t is the temperature (°C). The constants a and b are listed in Table V. In Figures 6 and 7, the constants a and b are plotted against the fraction of phenyl in the respective polymer, x_{Ph}. While the constant a displays a monotonous change with x_{Ph}, the constant b for OV 25 deviates markedly from the tendency seen in the other polymers. Further, with OV 25, the plot in Figure 5 deviates significantly from linearity. The cause of these features is not known, although the uncertainty in the specific volume of the polymer may be partly responsible.

To conclude, it should be stressed that the PMPS–alkane interactions are solely due to dispersion forces. Therefore, the values of δ_2^2 obtained from the PMPS–alkane interaction parameters may be expected to be close to the true cohesive energy densities of the respective polymers. The δ_2 values derived from polar solute–PMPS interactions are likely to contain contributions of the polar forces that are absent from the polymer–polymer interactions and, thereby, from the cohesive energy density of PMPS.

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Registry No. OV 25, 76999-90-1; $H(CH_2)_5H$, 109-66-0; $H(CH_2)_6H$, 110-54-3; $H(CH_2)_8H$, 111-65-9; $H(CH_2)_9H$, 111-84-2; cyclohexane, 110-82-7.