to increase the occupation fraction significantly. Consequently, we were unable to determine t, but only K_b, which for the butyl polyampholyte in 0.004 M LiCl at pH values of 4.2, 6.8, and 8.2 amounted to 1.6×10^2, 2.5×10^2, and 2.0×10^2 M^{-1}, respectively.

The effect of lowering the molecular weight of the butyl polyampholyte on the NPN fluorescence is shown in Figure 6. The two low molecular weight samples are seen to display greatly reduced fluorescence compared to the high molecular weight sample, reflecting the relative abilities of these samples to bind NPN. This result corresponds to a similar molecular weight dependency found for the micelle content of the hydrolyzed parent butyl copolymers by means of potentiometric titrations.[4]

In summary, the fluorescence results show that the micelle formation of our polyampholytes depends strongly on the size of the alkyl group and also on the degree of polymerization. For the high molecular weight samples the break appears to lie between the propyl polyampholyte, which shows little, if any, tendency to micellize, and the butyl polyampholyte, which shows substantial micelle formation. A similar break was observed previously between the corresponding hydrolyzed parent copolymers. However, no break was detected in the molecular dimensions, as observed by means of the viscosity, between the propyl and butyl polyampholytes. This finding suggests that even at its isoelectric point the butyl polyampholyte is not a single hypercoiled micelle but consists of a randomly coiled assembly of small micelles.

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Static Investigation of the Influence of Polymer Molecular Weight and Loading in the Gas Chromatographic Determination of Poly(dimethylsiloxane) Interaction Parameters

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ABSTRACT: Activity coefficients and interaction parameters determined by a static method are reported for benzene and hexane at infinite dilution in five samples of poly(dimethylsiloxane) in the molecular weight range 3350–89000 at 303 K. A small but significant variation of these properties is shown to occur with benzene if the polymer loading on a relatively inert solid support is reduced below ca. 20 wt %. The variation is attributed to adsorption at the surface of the support and the gas–liquid interface. An appreciable variation of the solution properties with polymer molecular weight is found. However, this variation is not sufficient to explain the differences between results of other workers, which are probably best explained by difficulties in determining the amount of polymer used in the gas–liquid chromatographic measurements.

The technique of gas–liquid chromatography (GLC) has proved useful in the determination of thermodynamic properties of nonelectrolyte liquid mixtures[1] and has been shown to be capable of providing information on a wide range of polymer properties including solution parameters.[2] Difficulties were experienced in dealing with a polymer stationary phase when the thermodynamic equations developed for GLC were applied to determine the activity coefficient of a volatile solute at infinite dilution in the stationary liquid phase, but ways of overcoming these have been described.[3] Summers, Tewari, and Schreiber[4] found good agreement between their infinite dilution activity coefficients and derived interaction parameters for various hydrocarbons in poly(dimethylsiloxane) (PDMS) measured by GLC and those from the static measurements of Chahal, Kao, and Patterson.[5] However, Lichtenthaler et al.[6] reported significant differences between static and GLC results and also between GLC determinations on the same polymer samples in an interlaboratory comparison.[7] A previous publication[8] showed that infinite dilution activity coefficients and interaction parameters measured by static and gas chromatographic methods for a number of hydrocarbon solutes with the same PDMS sample did agree within experimental error and suggested that differences in the results of other workers might well have arisen from difficulties in determining the amount of polymer present, as had been suggested earlier.[9] Two other factors that could have contributed to these differences are the polymer molecular weight and the ratio of polymer to solid support used in the GLC determinations.

The question of whether results obtained on a thin film of supported polymer represent the properties of bulk polymer has been examined by several workers. Lichtenthaler et al.[10] found significant differences between results obtained using a capillary column, with greater film thicknesses, and those on a packed column and doubted whether the latter represented interactions in the bulk polymer. Braun and Guillet[11] ascribed the differences to kinetic factors rather than to the presence of different sorption processes. The polymer loading, that is the amount of sample that is polymer, has been shown to be important in a number of studies,[12,13] and this paper describes its influence on the solution properties determined for benzene in PDMS.

Although there have been many studies of the thermodynamic properties of PDMS solutions, few of these have considered the effect of polymer molecular weight. Using GLC, Deshpande et al.[14] found appreciable differences in interaction parameters for two samples of PDMS, which they ascribed to molecular weight. Similarly, Galin[15] found

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Table I
Properties of the Polymers at 303 K

polymer	mol wt	density, g cm^{-3}
PDMS I	3 350	0.9523
PDMS II	6 650	0.9571
PDMS III	15 650	0.9618
PDMS IV	26 000	0.9643
PDMS V	89 000	0.9654

variation of GLC retention volumes in the molecular weight range 3700–30 000. Conversely, Muramoto,[16] using a static method, reported the interaction parameter for methyl ethyl ketone in PDMS to be independent of molecular weight above a value of 4600. In order to investigate any possible effects, activity coefficients were determined in this work for benzene and hexane in PDMS samples of molecular weights in the range 3350–89 000.

Experimental Section

Apparatus. Absorption isotherms for benzene and hexane in each polymer sample were determined by using a Sartorius Model 4102 electronic vacuum microbalance in conjunction with a Texas Instruments quartz Bourdon pressure gauge with a 1000-torr range. The balance was operated at 10 times the basic range allowing a total weight change of 200 mg to be monitored with a precision of 0.01 mg on a sample weight of ca. 1.8 g. Weight changes and pressure measurements are believed to have been accurate to ±0.01 mg and ±0.01 torr, respectively. The apparatus and techniques have been described previously.[17] The temperature at which the isotherms were recorded was monitored by using a mercury-in-glass thermometer that had been calibrated with a platinum resistance thermometer and was controlled at 302.99 ± 0.01 K.

Materials. The benzene and hexane were high-purity (99.99%) samples from the National Physical Laboratory, England, and were handled throughout under vacuum. The solid support was a Phase Separations Ltd. Celite 545 AW diatomaceous earth of 100–120 mesh size. The PDMS samples were Dow Corning Ltd. DC200 silicone fluids, having viscosities of 50, 100, 350, 1000, and 12 500 cSt and are designated PDMS I–PDMS V in order of ascending molecular weight. Each sample was used as received except the last, which was treated to remove low molecular weight material by using the procedure of Crescenzi and Flory.[18] To ensure that the weight of polymer in each absorbent sample was known accurately, the polymer was weighed directly into the balance sample bucket containing the required amount of solid support to give the desired polymer-to-support ratio. The polymer was then dispersed on the solid with ethyl acetate, which was then removed by evaporation.

The density of the highest molecular weight polymer (PDMS V) was assumed to conform to the relation determined by Shih and Flory,[19] and its number-average molecular weight was determined by measurement of its intrinsic viscosity in toluene[20] at 25 °C and application of the relation of Barry.[21] The densities of the other polymers were determined by using density bottles calibrated with water and triply distilled mercury at 302.99 ± 0.02 K, and their number-average molecular weights were determined by measurement of their bulk viscosities at 25 °C using an NPL calibrated kinematic viscometer and Barry's relation.[21] The polymer properties are shown in Table I.

Results and Discussion

The difficulties of using Raoult's Law activity coefficients with the uncertainties in molecular weight when polymers are used[3] were circumvented by calculating activity coefficients for the volatile components ${}^{v}\gamma_1$ on the basis of volume fractions ϕ_i by using the equation

$$\ln {}^{v}\gamma_1 = \ln [P_1/(P_1^0\phi_1)] + [(V_1^0 - B_{11})(P_1^0 - P_1)/RT] + [(B_{11}/RT)^2((P_1^0)^2 - P_1^2)/2] \quad (1)$$

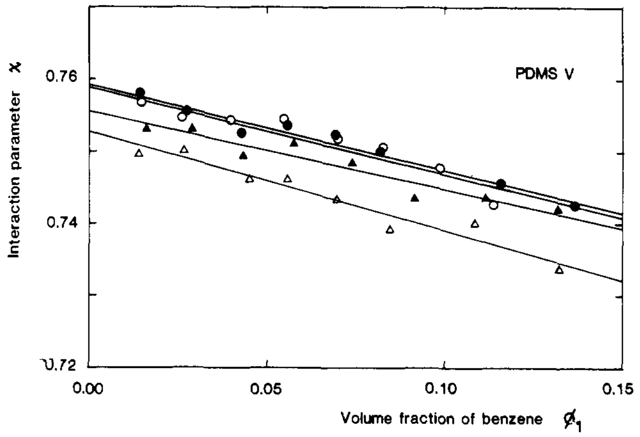

Figure 1. Interaction parameter χ for benzene in PDMS V at 303 K plotted against benzene volume fraction ϕ_1 for various polymer loadings. The wt % polymer loadings on Celite are 28.84 (●), 20.31 (○), 9.34 (▲), and 6.22 (△).

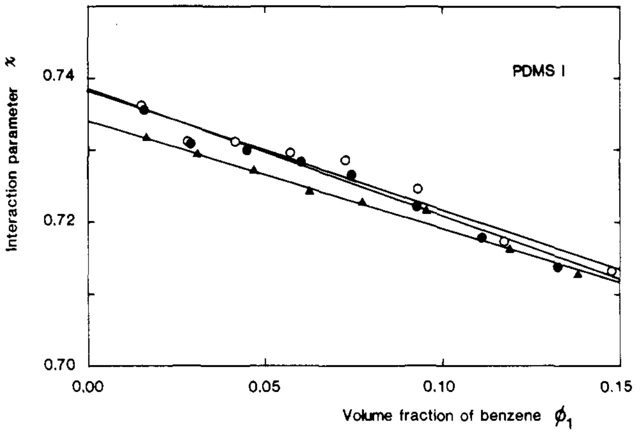

Figure 2. Interaction parameter χ for benzene in PDMS I at 303 K plotted against benzene volume fraction ϕ_1 for various polymer loadings. The wt % polymer loadings on Celite are 29.92 (●), 20.13 (○), and 10.21 (▲).

A saturated vapor pressure P_1^0 of 185.86 torr,[22] a second virial coefficient B_{11} of −1.845 dm^3 mol^{-1},[23] and a molar volume V_1^0 of 132.54 cm^3 mol^{-1}[24] were used for hexane. The corresponding values for benzene were 118.76 torr,[22] −1.492 dm^3 mol^{-1},[23] and 89.95 cm^3 mol^{-1},[25] respectively. Interaction parameters χ were calculated from the Flory–Huggins expression[26]

$$\ln {}^{v}\gamma_1 = (1 - 1/r)(1 - \phi_1) + (1 - \phi_1)^2\chi \quad (2)$$

where ϕ_1 is the absorbate volume fraction and r is the ratio of the molar volumes of the components.

Variation of Benzene Interaction Parameter with Polymer Loading. Of the hydrocarbon–PDMS systems studied previously,[8] is was thought that benzene would exhibit the greatest adsorption effects. The magnitude of the possible effects was investigated by determining absorption isotherms for benzene in the highest and lowest molecular weight PDMS samples over a range of polymer loadings. Loadings are quoted throughout as percentages by weight of the absorbent sample that was polymer. The absorption isotherms are tabulated in terms of volume fraction activity coefficients in Table II, except that for PDMS V at 20% loading which was reported previously (see run A, Table III, ref 8). The derived interaction parameters are shown plotted against volume fraction of benzene in Figures 1 and 2. The isotherms recorded for each polymer with loadings ≥20% agree within experimental error and show that bulk solubility was the major sorption process and that any adsorption effects were negligible. However χ values from the approximately 10% and 6% loaded samples were significantly lower. The

Table II
Absorption of Benzene by PDMS at 303 K at Various Polymer Loadings

PDMS I loading								
10.21%			20.13%			29.92%		
ϕ_1	P_1, torr	$\ln {}^{v}\gamma_1$	ϕ_1	P_1, torr	$\ln {}^{v}\gamma_1$	ϕ_1	P_1, torr	$\ln {}^{v}\gamma_1$
0.0165	10.24	1.6648	0.0148	9.3	1.6744	0.0157	9.82	1.6709
0.0307	18.42	1.6286	0.0278	16.81	1.6385	0.0286	17.26	1.6350
0.0469	27.02	1.5880	0.0413	24.19	1.6062	0.0445	25.82	1.5969
0.0625	34.61	1.5493	0.0569	32.15	1.5677	0.0602	33.67	1.5578
0.0774	41.41	1.5132	0.0728	39.56	1.5299	0.0741	40.06	1.5237
0.0954	48.94	1.4713	0.0929	48.13	1.4799	0.0923	47.79	1.4804
0.1184	57.46	1.4148	0.1173	57.16	1.4191	0.1109	54.78	1.4326
0.1382	64.05	1.3682	0.1474	67.03	1.3493	0.1316	61.84	1.3822
PDMS V loading								
6.22%			9.34%			28.84%		
ϕ_1	P_1, torr	$\ln {}^{v}\gamma_1$	ϕ_1	P_1, torr	$\ln {}^{v}\gamma_1$	ϕ_1	P_1, torr	$\ln {}^{v}\gamma_1$
0.0139	9.09	1.7137	0.0160	10.41	1.7120	0.0146	9.56	1.7206
0.0267	16.90	1.6838	0.0291	18.34	1.6798	0.0275	17.46	1.6853
0.0451	27.22	1.6341	0.0435	26.40	1.6414	0.0430	26.23	1.6450
0.0559	32.88	1.6079	0.0578	33.97	1.6082	0.0560	33.10	1.6146
0.0702	39.78	1.5715	0.0741	41.81	1.5667	0.0693	39.70	1.5815
0.0852	46.48	1.5323	0.0919	49.52	1.5202	0.0817	48.20	1.5344
0.1086	56.15	1.4786	0.1115	57.45	1.4745	0.1162	59.30	1.4651
0.1326	64.61	1.4185	0.1321	64.88	1.4259	0.1364	66.37	1.4165

Table III
Effect of Polymer Loading on Infinite Dilution Properties of Benzene in PDMS at 303 K

PDMS I			PDMS V		
% loading	$\ln {}^{v}\gamma_1^{\infty}$	χ^{∞}	% loading	$\ln {}^{v}\gamma_1^{\infty}$	χ^{∞}
29.92	1.7127	0.7385	28.84	1.7581	0.7591
20.13	1.7119	0.7383	20.31	1.7578	0.7588
10.21	1.7074	0.7340	9.34	1.7543	0.7553
			6.22	1.7518	0.7528

interaction parameters are believed to be accurate to 0.002–0.004 depending on the concentration and system involved. The variation of χ with loading was of a similar magnitude for both polymers. The variation of interaction parameter with concentration was found to obey a linear relation of the form

$$\chi = \chi^{\infty} + \chi'\phi_1 \tag{3}$$

In eq 3, χ^{∞} represents the interaction parameter at infinite dilution of the volatile component and allows calculation of ${}^{v}\gamma_1^{\infty}$, the volume fraction activity coefficient at infinite dilution. This is the solution thermodynamic property usually measured by GLC where low polymer loadings are often employed. The results from the present work extrapolated to infinite dilution are shown in Table III, and it can be seen that small, but significant, differences can be caused by using low polymer loadings to measure solution properties. It is interesting to note that the χ^{∞} value of 0.7528 obtained in this work with PDMS V for the 6% loaded sample shows excellent agreement with the value of 0.752 obtained previously by GLC with a 4–8% loaded column.[8] Summers et al.[4] using GLC detected no variation in χ^{∞} for benzene in PDMS with loadings >7.7% but found that a 6.2% loaded column yielded significantly lower results. They attributed this to adsorption of benzene onto exposed solid support despite finding no retention of benzene on a column of bare support. Their results were quoted to a precision of 1%, which would not be sufficient to detect the variation found in the present work for loadings between 10 and 20%.

At a relative vapor pressure (P_1/P_1^0) of 0.53 the uptake of benzene by PDMS I was 138 mg/g of polymer for the 30% loaded sample but 146.5 mg g^{-1} for the 10% sample. For the weight of PDMS in the 10% sample this leads to an "excess absorption" of about 1.4 mg which may be attributed to adsorption. An isotherm recorded at the same temperature by using bare Celite showed an adsorption of 0.28 mg of benzene per gram of Celite at a relative pressure of 0.5. Thus, for the amount of Celite present in the 10% sample the maximum uptake by the support could have been in the region of 0.5 mg, which is insufficient to account for the total weight of adsorbed benzene. Thus, it seems that the variation in results with polymer loading is caused not only by adsorption onto the solid support but also by adsorption at the gas–liquid interface, a phenomenon that is well-known in GLC.[1]

Variation of Benzene and Hexane Interaction Parameters with Polymer Molecular Weight. The effect of polymer molecular weight on measured activity coefficients and interaction parameters was investigated by recording isotherms for the absorption of hexane and benzene by the five polymers at 20% loadings. The absorption isotherms for hexane have been published previously,[27] while those for benzene with PDMS II, III, and

Table IV
Absorption of Benzene by PDMS at 303 K of Various Molecular Weights at Approximately 20% Polymer Loading

PDMS II			PDMS III			PDMS IV		
ϕ_1	P_1, torr	$\ln {}^{v}\gamma_1$	ϕ_1	P_1, torr	$\ln {}^{v}\gamma_1$	ϕ_1	P_1, torr	$\ln {}^{v}\gamma_1$
0.0144	9.21	1.6915	0.0152	9.84	1.7049	0.0145	9.43	1.7120
0.0298	18.29	1.6531	0.0297	18.43	1.6648	0.0283	17.79	1.6764
0.0439	25.96	1.6147	0.0419	25.24	1.6337	0.0434	26.19	1.6365
0.0568	32.60	1.5847	0.0546	31.90	1.6029	0.0550	32.37	1.6093
0.0717	39.64	1.5464	0.0704	39.53	1.5622	0.0692	39.31	1.5731
0.0904	47.73	1.5002	0.0887	47.57	1.5160	0.0890	48.05	1.5217
0.1099	55.50	1.4540	0.1075	55.16	1.4711	0.1078	55.62	1.4760
0.1314	62.94	1.4015	0.1291	62.87	1.4179	0.1304	63.75	1.4215

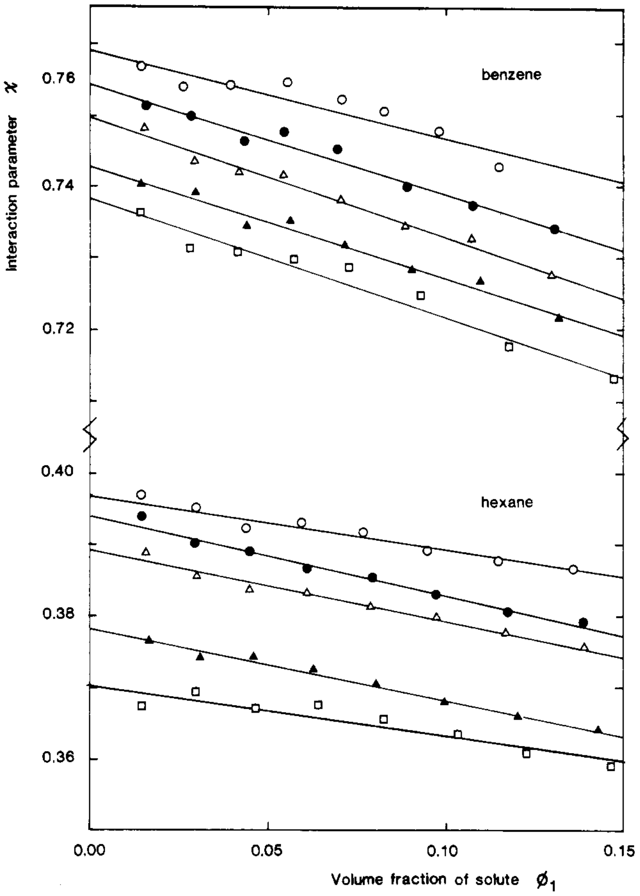

Figure 3. Interaction parameter χ for benzene and hexane in PDMS of various molecular weights at 303 K plotted against solute volume fraction ϕ_1: PDMS V (○), PDMS IV (●), PDMS III (△), PDMS II (▲), and PDMS I (□).

Table V
Effect of Polymer Molecular Weight on Infinite Dilution Properties of PDMS at 303 K

	hexane		benzene	
polymer mol wt	${}^{v}\gamma_1^{\infty}$	χ^{∞}	${}^{v}\gamma_1^{\infty}$	χ^{∞}
3 350	3.720	0.3704	5.540	0.7383
6 650	3.891	0.3780	5.639	0.7429
15 650	3.980	0.3893	5.721	0.7469
26 000	4.011	0.3939	5.760	0.7543
89 000	4.036	0.3965	5.799	0.7588

IV are listed in Table IV, with PDMS I in Table II and PDMS V published previously (see run A, Table III, ref 8). A plot of the interaction parameters vs. solute volume fraction is presented in Figure 3 and shows that appreciable differences can be caused by variation in the polymer molecular weight. The results extrapolated to infinite dilution are given in Table V and show that in the molecular weight range examined, a variation of 0.02–0.025 in χ^{∞} is found, which is well outside the experimental error of the measurements. Most of the studies by other workers, discussed earlier, involved PDMS of molecular weights in the range 3×10^4 to 5×10^5. The results in Table V show that for molecular weights in this range only a very small increase in χ^{∞}, of the order of the experimental error, would be expected. Thus the variation is not sufficient to explain the differences between results obtained by other workers, which are probably best explained by previous suggestions of difficulties in determining the amount of polymer used in the GLC measurements.

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Registry No. Benzene, 71-43-2; hexane, 110-54-3.

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