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Thermodynamic Study of Heptane + Silicone Mixtures. Excess Volumes and Enthalpies at 298.15 K

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S *Supporting Information*

ABSTRACT: Excess molar volumes V^E and partial molar enthalpies and excess enthalpies H^E of binary mixtures of heptane + linear (hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, dodecamethylpentasiloxane) and cyclic (octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane) silicone oligomers have been determined at 298.15 K. Both excess properties have small values ($|V^E| < 0.13\ \mathrm{cm^3 \cdot mol^{-1}}$, $H^E < 0.23\ \mathrm{kJ \cdot mol^{-1}}$) for linear silicones, exhibiting a monotonic increase with an increasing number of dimethylsiloxane units. Higher V^E and H^E data are instead observed in the case of cyclic molecules, with a larger value exhibited by octamethylcyclotetrasiloxane. Partial molar volumes at infinite dilution of silicones in heptane are markedly larger than those of *n*-alkanes of the same size. Likewise, their enthalpies of solvation in heptane are less negative than those of hydrocarbons. Cyclic silicones display partial molar volumes lower than corresponding linear compounds, and their solvation enthalpies are slightly more negative. Both partial molar volumes and enthalpies of solvation of silicones are found to be additive, thus enabling the prediction of these properties for unstudied molecules. The additivity of partial molar volumes was found to also hold for a short silicone polymer, thus indicating an open structure of the polymeric chain in hydrocarbon solution, that is, equally exposed to the solvent as the shorter oligomers.

INTRODUCTION

In recent years, we have studied the thermodynamic properties of a series of multicomponent mixtures of a variety of organic compounds. In fact, the availability of sets of thermodynamic data such as G^E, H^E, V^E, and C_p^E is of great importance for understanding the molecular interactions among the mixture components and for their modelization. Particular attention in the literature was devoted to mixtures of alkanes with different categories of monofunctional organic compounds, owing to the reasonable choice of the hydrocarbons as a convenient reference term for discussing the effect of different polar groups. Our most recent papers dealt with the measurements of excess volumes, V^E,[1,2] and excess enthalpies, H^E,[3,4] of binary mixtures of *n*-heptane with linear and cyclic primary, secondary, and tertiary amines.

In this paper, we report V^E and H^E for some binary mixtures of *n*-heptane with linear and cyclic silicones, also called polydimethylsiloxanes. The general structures for the linear and cyclic siloxanes are $Me(Me_2SiO)_nSiMe_3$ and $(Me_2SiO)_n$, respectively. Four linear silicones with $n = 1$ to 4, hexamethyldisiloxane (MM), octamethyltrisiloxane (MDM), decamethyltetrasiloxane (MD_2M), and dodecamethylpentasiloxane (MD_3M), and two cyclic silicones with $n = 4$ and 5, octamethylcyclotetrasiloxane (D_4) and decamethylcyclopentasiloxane (D_5), have been investigated. A few measurements of V^E have been also carried out on mixtures of a low molecular weight linear polymer, that is, trimethylsilyl-terminated polydimethylsiloxane (PDMS, MW = 2000). The abbreviations M and D are based on the Hurd notation.[5]

Silicones are known for their outstanding properties such as high thermal stability, thermal resistance, dielectric properties, film forming ability, surface activity, and hydrophobicity.[6] Such properties suggested their use in a variety of industrial and consumer product applications, including lubricants, automotive, aquarium joints, electronics, building constructions, sealants, antifoam agents, polishes, waxes, and personal care (hair conditioners, shampoos, skin lotions). In biomedical applications silicones have been used in devices such as breast implants and catheters[6] and in vitreoretinal surgery as vitreous substitutes.[7,8] They also deserve theoretical interest. Their mixtures with hydrocarbons were considered a good model for testing a phenomenological corresponding state principle[9] or the application of the Prigogine−Flory theory to mixtures of small molecules[10] and polymers.[11]

The peculiar properties of silicones are due, at least in part, to the structure of the main chain consisting of repeat units Me_2SiO. As illustrated in Figure 1, the skeleton of dimethylsiloxanes is made of silicon and oxygen atoms, but the external surface of both linear and cyclic molecules is mainly constituted by methyl groups which almost completely prevent Si and O atoms from contact with the solvent. For comparison, Figure 1 also shows the structure of the linear alkane C14.

From the present experimental results and literature data, the partial molar quantities and the solvation enthalpies at infinite dilution of the silicones in heptane have been calculated. The behavior of these quantities has been compared with the corresponding quantities of hydrocarbons in mixtures with

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n-alkanes, using the intrinsic volume as a molecular descriptor. As already done for other categories of organic compounds,[1−4] the effects of chain lengthening, cyclization, and branching have been discussed.

■ EXPERIMENTAL SECTION

Materials. All organic chemicals were high-purity reagents and were used without further purification. Sources and purity are listed in Table 1, together with density (reported as molar volume) measured by us, and other relevant physicochemical properties. The purity was checked by gas chromatography and water content by Karl Fischer analysis. No significant difference was found with respect to the impurity content declared by factories.

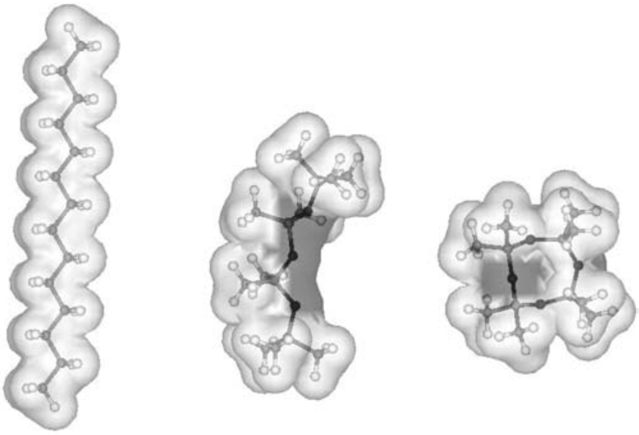

Figure 1. Representation by DS ViewerPro 5.0 (external molecular surface obtained by van der Waals radii) of n-tetradecane, MD_2M, and D_4.

As illustrated in previous works on V^E [1,17] and H^E,[3,18] the purity of substances is not a crucial requirement in excess properties measurements. We found that when the impurities are chemically similar to the substance they contaminate, as is usually the case, the value of the systematic error caused in the excess property is less than the mass fraction impurity content. The same holds for errors in the heats of solution. This is confirmed by the close similarity of two sets of V^E and H^E results obtained using two samples of the same silicone (MM) coming from two different factories, respectively, and characterized by different purity degrees.

Density Measurements. Density measurements were carried out by means of an Anton Paar vibrating-tube densimeter (DMA 60/602) operating in the static mode and capable of a precision of better than $3 \cdot 10^{-6}\ \mathrm{g \cdot cm^{-3}}$. Temperature control inside the oscillation chamber (± 0.001 K), calibration, and test of the apparatus were described in detail elsewhere.[19,20] Details of the experimental procedure, including vapor phase corrections and accuracy of measurements, were also reported recently.[1] Activity coefficients of the components, necessary to calculate vapor phase corrections, were found in the literature only for mixtures of MM with n-hexane.[21] However, the use of these activity coefficients for all mixtures investigated yielded corrections to the mole fraction, x, and V^E much lower than experimental precision.

The accuracy on molar volumes V^* is estimated to be better than $0.001V^*$, as suggested by the close similarity of our V^* and those of literature (see Table 1). The combined expanded uncertainty in V^E and V^E/x_1x_2, due to density and mole fraction errors, was usually <0.008 and <0.05 $\mathrm{cm^3 \cdot mol^{-1}}$, respectively.

Table 1. Source, Purity, Molar Volume, V^*, van der Waals Volume, V_w, Vapor Pressure, p^*, and Enthalpy of Vaporization, $\Delta_{vap}H°$, of Pure Liquids at 298.15 K

			V^{*b}	V_w	p^*	$\Delta_{vap}H°$
chemical name[a]	source	initial mass fraction purity	$\mathrm{cm^3 \cdot mol^{-1}}$	$\mathrm{cm^3 \cdot mol^{-1}}$	kPa	$\mathrm{kJ \cdot mol^{-1}}$
heptane	Fluka	>0.995	147.44^{c}	77.61	6.09^{m}	36.66^{p}
		water <0.0005				
MM	Aldrich	0.995	213.94^{d}	108.3	$5.50^{n,o}$	37.60^{q}
	Fluorochem	0.98	214.04^{d}			
MDM	Aldrich	0.98	290.35^{e}	151.3	1.3^{n}	49.43^{r}
MD_2M	Fluka	0.97	366.25^{f}	194.2	0.3^{n}	62.30^{r}
TM_3			367.85^{g}	195.2		60.10^{r}
MD_3M	Aldrich	0.97	442.40^{h}	237.2	0.07^{n}	75.16^{r}
QM_4			446.90^{g}	237.2		71.04^{r}
MD_4M			518.50^{i}	280.2		
PDMS	Fluorochem MW 2000 Viscosity 20 cst		2106.90			
D_3				128.9		45.65^{r}
D_4	Fluka	0.99	312.12^{j}	171.8	0.12^{n}	$57.77^{r,s}$
D_5	Fluka	0.97	388.93^{k}	214.8	0.03^{n}	68.47^{r}
D_6			462.47^{l}	257.8		

[a] MM = hexamethyldisiloxane, MDM = octamethyltrisiloxane, MD_2M = decamethyltetrasiloxane, MD_3M = dodecamethylpentasiloxane, MD_4M = tetradecamethylhexasiloxane, D_3 = hexamethylcyclotrisiloxane, D_4 = octamethylcyclotetrasiloxane, D_5 = decamethylcyclopentasiloxane, D_6 = dodecamethylcyclohexasiloxane, TM_3 = methyl-tris(trimethylsiloxy)silane, QM_4 = tetrakis(trimethylsiloxy)silane, PDMS = polydimethylsiloxane; $M = Me_3SiO_{1/2}$; $D = O_{1/2}Me_2SiO_{1/2}$; $T = MeSiO_{3/2}$; $Q = Si(O_{1/2})_4$. [b] The relative uncertainty is: $u_r(V^*) < 0.001$, for the data measured by us. [c] 147.48, ref 12. [d] 213.059, ref 12, 214.03 ref 5. [e] 289.773, ref 12, 290.35 ref 5. [f] 365.977, ref 12, 366.18 ref 5. [g] Reference 13. [h] 442.22, ref 12, 442.07, ref 5. [i] Reference 12; 518.03, ref 5. [j] 312.16, ref 5. [k] 388.02, ref 5. [l] Reference 5. [m] Reference14. [n] Reference 15. [o] 5.56, ref 14. [p] Reference 16. [q] Calculated from data of ref 15; 38.20 from ref 15. [r] Calculated from data of ref 15. [s] 60.08, calculated from data of ref 14.

Table 2. Experimental Densities and Excess Volumes of Mixing of Heptane (1) + Silicone (2) at 298.15 K[a]

x_1	ρ / $g \cdot cm^{-3}$	V^E / $cm^3 \cdot mol^{-1}$	x_1	ρ / $g \cdot cm^{-3}$	V^E / $cm^3 \cdot mol^{-1}$	x_1	ρ / $g \cdot cm^{-3}$	V^E / $cm^3 \cdot mol^{-1}$	x_1	ρ / $g \cdot cm^{-3}$	V^E / $cm^3 \cdot mol^{-1}$
					Heptane (1) + MM (2)						
0.0541	0.755739	−0.025	0.3131	0.740108	−0.088	0.6792	0.712196	−0.096	0.9237[b]	0.688293	−0.030
0.0752[b]	0.754911	−0.034	0.3968[b]	0.734608	−0.091	0.7073[b]	0.709822	−0.092	0.9528	0.685051	−0.019
0.1111[b]	0.752852	−0.040	0.4121	0.733315	−0.099	0.7762	0.703316	−0.080	0.9606	0.684173	−0.015
0.1978	0.747433	−0.069	0.4936[b]	0.727502	−0.095	0.8013[b]	0.700937	−0.064	0.9737	0.682692	−0.010
0.1982[b]	0.747692	−0.065	0.4957	0.727168	−0.102	0.8729	0.693665	−0.049			
0.2921[b]	0.741746	−0.082	0.5892	0.719797	−0.098	0.8956[b]	0.691309	−0.037			
					Heptane (1) + MDM (2)						
0.0564	0.810669	0.009	0.3923	0.781292	0.015	0.7021	0.741134	−0.003	0.9650	0.688644	0.005
0.1114	0.806583	0.003	0.5037	0.768701	0.016	0.7983	0.724530	−0.002	0.9766	0.685727	0.005
0.1941	0.799935	0.008	0.5051	0.768580	0.002	0.9019	0.703487	−0.001	0.9882	0.682750	0.004
0.2931	0.791152	0.012	0.5940	0.757125	−0.000	0.9510	0.692081	0.005			
					Heptane (1) + MD_2M (2)						
0.1064	0.840482	0.043	0.5101	0.798198	0.094	0.8042	0.742915	0.078	0.9556	0.696991	0.028
0.2143	0.831452	0.063	0.5974	0.784931	0.092	0.904	0.714649	0.051	0.9704	0.691463	0.018
0.3096	0.822306	0.075	0.6128	0.782373	0.089	0.9536	0.697736	0.026	0.9851	0.685736	0.008
0.4037	0.811915	0.092	0.7039	0.765519	0.088						
					Heptane (1) + MD_3M (2)						
0.0947	0.863405	0.048	0.4032	0.834674	0.107	0.7037	0.785543	0.095	0.9043	0.725311	0.050
0.1982	0.855262	0.077	0.5016	0.821820	0.111	0.8012	0.760549	0.084	0.9504	0.705289	0.031
0.2985	0.846075	0.088	0.6056	0.805184	0.108						
					Heptane (1) + PDMS (2)						
0.5022	0.931341	0.173	0.6013	0.923444	0.082	0.8981	0.846314	0.042	0.9613	0.778142	−0.006
					Heptane (1) + D_4 (2)						
0.0573	0.942470	0.101	0.4013	0.883659	0.442	0.8312	0.759623	0.328	0.9598	0.701242	0.103
0.1122	0.934534	0.175	0.5287	0.854726	0.490	0.9054	0.727727	0.216	0.9730	0.694360	0.071
0.2048	0.920026	0.289	0.6210	0.830427	0.459	0.9515	0.705461	0.125	0.9860	0.687386	0.039
0.3094	0.901732	0.385	0.7084	0.803913	0.435						
					Heptane (1) + D_5 (2)						
0.1411	0.936914	0.133	0.4981	0.877750	0.23	0.7773	0.796525	0.235	0.9101	0.735622	0.14
0.2809	0.917473	0.189	0.5974	0.853877	0.263	0.8618	0.760263	0.178	0.9566	0.708605	0.069
0.3875	0.899704	0.220	0.6967	0.824976	0.257						

[a] Standard uncertainties u are: $u(T) = 0.02$ K, $u(x) = 0.0003$, $u(\rho) = 5 \cdot 10^{-6}$ $g \cdot cm^{-3}$; the combined expanded uncertainty U_c is: $U_c(V^E) = 0.008$ $cm^3 \cdot mol^{-1}$ (level of confidence = 0.95). [b] These mixtures were prepared with MM from Aldrich; the other from Fluorochem.

Calorimetric Measurements and Data Treatment. Heats of solution were collected through a heat flow calorimeter (thermal activity monitor model TAM 2277) from Thermometric, Sweden. Experiments were conducted by adding a pure component, via Hamilton gas-tight syringes of capacity ranging from (100 to 1000) μL driven by Lund syringe pumps model 6120, to an ampule of (20 or 4) cm^3 capacity initially charged with the other component or with a stock mixture of them. With this system, we were able to make accurate injections starting from a minimum volume of 1 μL, with a precision of 0.005 volume, and to measure accurate heat effects as small as 0.01 J, with a sensitivity of 0.5 μW on the heat flow. The apparatus, the experimental procedure, and the data treatment have been described exhaustively in previous papers.[3,4] Here we limit information to basic hints on the data treatment given below.

The experimental solution heats, Q_{exp}, released by the additions of very small quantities of the titrant, n_j, practically represent partial molar enthalpies, $\overline{H}_j$ ($\overline{H}_j \cong Q/n_j$). Calculated values of the solution heats, Q_{calc}, can be obtained by proper differentiation of the equation $H^E = f(x)$, such as the Redlich–Kister (RK) one,

$$Z^E = x_1 x_2 \sum_{k=1}^{n} c_k (x_1 - x_2)^{k-1} \tag{1}$$

where $Z = H$. A standard least-squares procedure identifies the best values of c_k parameters at the minimum of the objective function (OF = $\Sigma(Q_{exp} - Q_{calc})^2$). Proper allowance was made for the heat involved in the phase composition changes brought about by the vapor–liquid equilibration after each addition. Since in this technique the direct experimental measurements and the fitted quantities are heats of solution, the $\overline{H}_j$, and in particular the partial molar enthalpy at infinite dilution, H_j°, are

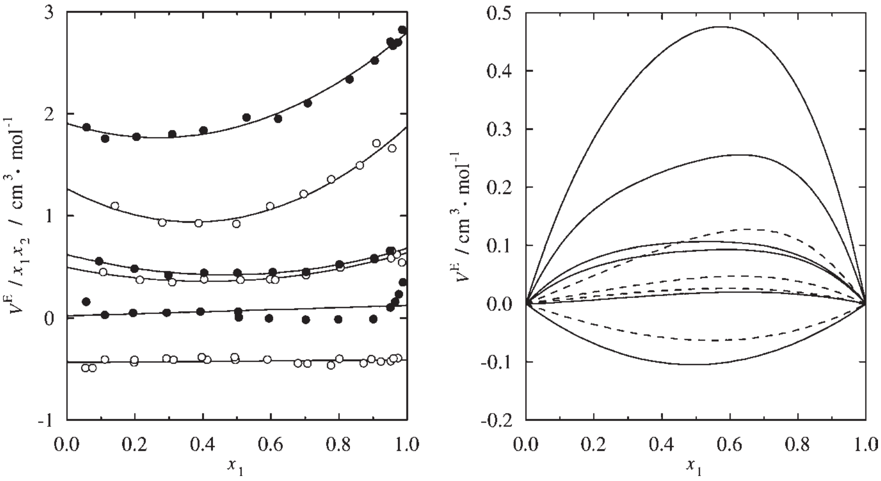

Figure 2. Excess molar volumes, V^E/x_1x_2 (left panel) and V^E, of heptane (1) + silicone (2) mixtures vs mole fraction x_1. ○, ●, experimental points from Table 2; —, curves calculated with parameters of Table 3, from top to bottom: D$_4$, D$_5$, MD$_3$M, MD$_2$M, MDM, MM; - - -, curves calculated from data of ref 22, from top to bottom: MD$_3$M, MD$_2$M, MDM, MM.

Table 3. Parameters c_k of Equation 1 ($Z = V$), Standard Deviations of the Fit, σ, Excess Volumes at Equimolar Composition, V^E ($x = 0.5$), Partial Specific Volumes, V_{2sp}°, Excess Partial Molar Volumes, $V_i^{E,\circ}$, and Partial Molar Volumes at Infinite Dilution, V_2°, for Binary Heptane (1) + Silicone (2) Mixtures at 298.15 K[a]

	c_1	c_2	c_3	$\sigma(V^E/x_1x_2)$	$\sigma(V^E)$	$V^E(x = 0.5)$	$V_1^{E,\circ}$	$V_2^{E,\circ}$	V_2°	V_{2sp}°
component 2	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^3·g^{-1}
MM	−0.41802	0.01500		0.031	0.005	−0.105	−0.43	−0.40	213.57	1.3153
MDM	0.07355	0.05122		0.103	0.012	0.018	0.02	0.13	290.48	1.2280
MD$_2$M	0.36695	0.07199	0.20182	0.035	0.003	0.092	0.50	0.64	366.89	1.1809
MD$_3$M	0.42528	0.03043	0.22793	0.021	0.004	0.106	0.62	0.68	443.08	1.1513
PDMS	0.51282			0.420	0.038	0.128		0.51	2107.41	1.0537
D$_4$	1.87170	0.44675	0.48023	0.047	0.008	0.468	1.91	2.80	314.92	1.0617
D$_5$	0.97999	0.30461	0.59005	0.057	0.008	0.245	1.27	1.88	390.81	1.0540

[a] The combined expanded uncertainties U_c are: $U_c(V^E, x = 0.5) = 0.010$ cm^3·mol^{-1}; $U_c(V_i^{E,\circ}) = 0.08$ cm^3·mol^{-1}, $U_c(V_2^\circ) \cong 0.1$ cm^3·mol^{-1} (level of confidence = 0.95).

by far more precise than those that would be obtained from the direct H^E measurements by means of mixing-flow calorimetry.

The uncertainty in the observed heat, Q, as determined by the reproducibility of the experiment and by integration of the peak area, can be evaluated as $0.005Q$, which leads to an analogous uncertainty in the partial molar enthalpy. From σ's of c_k parameters (not reported in Table 2) we have calculated the standard deviations on H^E and H_j°. They amount to ± 0.5 J·mol^{-1} for H^E of all mixtures except MD$_3$M, for which is about 3.8 J·mol^{-1}. Standard deviations on H_j° have been calculated as ≈ 6 J·mol^{-1}, except for MD$_3$M for which it is 40 J·mol^{-1}. For this latter system, we found particular difficulties in obtaining the high accuracy found for the other because of its very lengthy dissolution process.

■ RESULTS

Volumes. The experimental density and V^E data of the examined mixtures are collected in Table 2. As done in previous works of ours,[1,2] fitting to eq 1 ($Z = V$) has been made using the objective function OF = $\Sigma((V^E/x_1x_2)_{exp} - (V^E/x_1x_2)_{calc})^2$. Experimental points and best fitting curves are plotted in Figure 2, left panel; in the right panel the corresponding V^E curves are shown, together with literature data at 303.15 K.[22] These latter data show slightly asymmetric curves with extreme values shifted toward larger heptane contents. The largest discrepancy of V^E ($x = 0.5$) data, about 0.05 cm^3·mol^{-1}, is found for MM and MD$_2$M. The V^E parameters of the RK eq 1 and the excess partial molar volumes at infinite dilution of the single components, $V_i^{E,\circ}$, are collected in Table 3. Values of the limiting partial molar volumes, V_i°, of each component i can be obtained from

$$V_i^\circ = V_i^* + V_i^{E,\circ} \qquad (2)$$

Both the magnitude of V_i° and its variation with molecular structure mostly depend on V^*, the pure compound molar volume, since $V_i^{E,\circ}$ contributes less than $0.01V^\circ$. Therefore the accuracy of this quantity is practically the same as that of V^* (Table 1), which is usually better than $0.001V^*$.

Enthalpies. As explained in previous papers,[3,4] the calorimetric experimental procedure generates a large amount of experimental data (≈ 440 experimental points in this case), which are not worth an extensive tabulation herein. These data can be retrieved as Supporting Information or can be obtained from the authors.

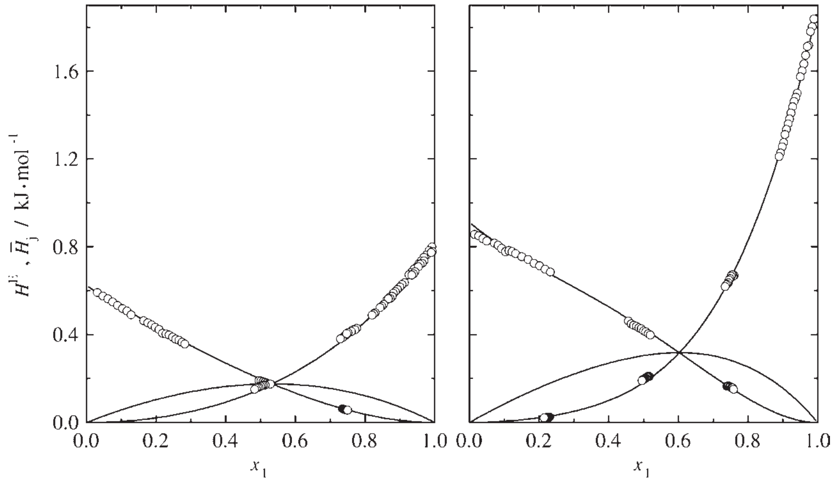

Figure 3. Excess enthalpies, H^E, and partial molar enthalpies, $\overline{H}_j$, for the binary mixtures heptane (1) + MM (2), left side, and heptane (1) + D_4 (2), right side. ○, experimental data; —, curves calculated with parameters of Table 4.

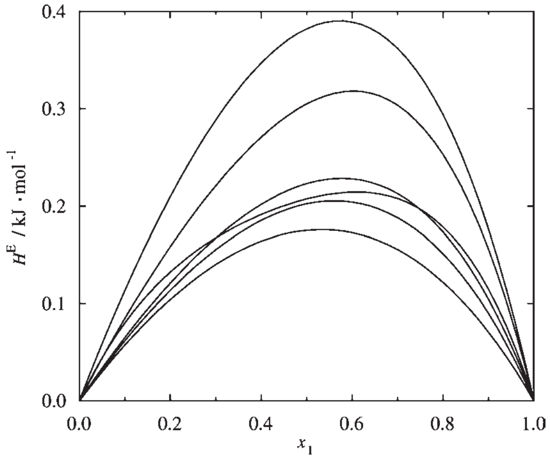

Figure 4. Excess molar enthalpies, H^E, of heptane (1) + silicone (2) mixtures vs mole fraction x_1. Curves calculated with parameters of Table 4, —, from top to bottom: D_4, D_5, MD_2M, MD_3M, MDM, MM.

An example of what our experimental enthalpy data look like is given in Figure 3, where the mixtures of heptane with MM and D_4 are shown. Plots of H^E for all mixtures investigated here are instead shown in Figure 4. To our knowledge, no direct enthalpic data can be found in the literature for comparison. However, from the accurate data by Tancrède et al.[23] on excess enthalpies of mixtures of silicones with several linear hydrocarbons except for *n*-heptane, we can calculate the average H^E ($x = 0.5$) of the hexane and octane mixtures with MM, MD_2M, and D_4. The H^E difference with our values does not exceed 9 J·mol^{-1}, a very good agreement with our results (see Table 4).

The standard molar enthalpies of solvation in heptane, $\Delta_{\mathrm{solv}}H_2^\circ$, associated with the process: ideal gas → infinitely dilute solution, are reported in Table 4. They were obtained through the equation

$$\Delta_{\mathrm{solv}}H_2^\circ = H_2^\circ - \Delta_{\mathrm{vap}}H_2^\circ \qquad (3)$$

where H_2° is the excess partial molar enthalpy at infinite dilution of silicone and $\Delta_{\mathrm{vap}}H_2^\circ$ is its standard molar heat of vaporization. Vaporization enthalpies of silicones were calculated by us from vapor pressure data at different temperatures reported by Flaningam.[15] The magnitude of $\Delta_{\mathrm{solv}}H_2^\circ$, as well as its variation with molecular structure, depend mostly on $\Delta_{\mathrm{vap}}H_2^\circ$, the term H_2° contributing less than $0.05\Delta_{\mathrm{solv}}H_2^\circ$. Consequently, the uncertainty of this quantity is practically the same as that of $\Delta_{\mathrm{vap}}H_2^\circ$ (Table 1), which is estimated to not exceed ± 0.5 kJ·mol^{-1}.

■ DISCUSSION

Excess Quantities. By examining Figure 2, it can be noticed that all examined mixtures exhibit positive V^E's with the exception of heptane + MM. The largest V^E values are displayed by mixtures with cyclic silicones. In the series of linear silicones, the excess molar volumes of equimolar mixtures, $V^E(x = 0.5)$, are small and increase with increasing chain length from -0.1 cm^3·mol^{-1} for MM to 0.1 cm^3·mol^{-1} for MD_3M. Similarly, $V_1^{E,\circ}$ and $V_2^{E,\circ}$ increase with the increasing size of linear silicones.

The positive value of V^E (and $V_2^{E,\circ}$) is due to the destruction of dipolar interactions in neat silicones and, mostly, of the tight packing in the neat heptane. The observed V^E increase with silicone size suggests that the fitting of silicone molecules into the heptane structure is more and more sterically hindered as the size is increased. A similar positive contribution to V^E has been observed for mixtures of heptane with branched hydrocarbons and branched amines,[1] leading to larger V^E as the branching is increased. As a matter of fact, with the linear Si−O chains being fully methylated (Figure 1), silicones can be viewed as completely branched.

H^E results, shown in Figure 4, are all positive, slightly influenced by the size of the silicone component. The largest H^E are exhibited by mixtures with cyclic silicones. In the series of linear oligomers both H_1° and H_2° increase with increasing chain length of the silicone component (see Table 4).

Following the interpretation scheme proposed by Patterson,[24] the positive H^E and H_i° values can be qualitatively explained with a net destruction, in the mixing process, of the structural order present in the neat liquids (dipolar interactions and orientational order). The positive G^E [21] and V^E for the same systems can be explained likewise. The increasing trend of H^E and H_2° with silicone size, similarly to V^E, is to be ascribed to a positive contribution to H^E mainly due to a looser packing (and weaker

Table 4. Parameters c_k of Equation 1 ($Z = H$), Standard Deviations of the Fit, σ, Excess Enthalpies at Equimolar Composition, $H^E(x = 0.5)$, Excess Partial Molar Enthalpies, H_i°, and Solvation Enthalpies, $\Delta_{solv}H_2^\circ$, at Infinite Dilution for Binary Heptane (1) + Silicone (2) Mixtures at 298.15 K[a]

	c_1	c_2	c_3	$10^6 \cdot \sigma(Q)$	$H^E(x = 0.5)$	H_1°	H_2°	$\Delta_{solv}H_2^\circ$
component 2	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$
MM	0.70118	0.09207	0.01536	2.2	0.175, 0.172[b]	0.624	0.809	−37.39
MDM	0.80943	0.19525	0.05239	1.7	0.202	0.667	1.057	−48.37
MD_2M	0.89229	0.27207	0.07938	2.5	0.223, 0.214[b]	0.700	1.244	−61.06
MD_3M	0.82965	0.24034	0.39663	2.7	0.207	0.986	1.467	−73.69
D_4	1.52927	0.43820	0.12617	1.8	0.382, 0.377[b]	1.217	2.093	−55.68
D_5	1.22009	0.49249	0.18274	2.0	0.305	0.910	1.895	−66.58

[a] The combined expanded uncertainties U_c are: $U_c(H^E, x = 0.5) = 0.001\ \mathrm{kJ \cdot mol^{-1}}$; $U_c(H_i^\circ) = 0.01\ \mathrm{kJ \cdot mol^{-1}}$; $U_c(\Delta_{solv}H_2^\circ) = 0.5\ \mathrm{kJ \cdot mol^{-1}}$ (level of confidence = 0.95). [b] Value interpolated from data of mixtures with *n*-hexane and *n*-octane reported in ref 23.

interactions) of silicone molecules into the solvent as the size is increased.

Dilute Solutions. In the case of V^E, packing or void volume effects can prevail over structural order changes. Indeed, in a mixture of two species *i* and *j*, the V^E value is determined by different packing of *i* and *j* with respect to the pure liquids and also by the balance of the effects on V^E of *i*−*i*, *j*−*j*, and *i*−*j* interactions. On the contrary, the partial molar volume at infinite dilution, V°, besides the intrinsic volume of the solute, mostly reflects solute−solvent interactions and the closeness of the packing of the solvent molecules around the solute. For this reason, V° data lend themselves to an easier interpretation than V^E in terms of correlation between chemical structure and molecular interactions. Analogous considerations hold for H^E and the transfer enthalpy $\Delta_{solv}H_2^\circ$ of the solute molecule from the gaseous state to infinitely dilute solution.

Partial Molar Volumes. The volumetric behavior at infinite dilution in heptane for silicones and alkanes is presented in Figure 5 where the empty volume V_e, defined as

$$V_e = V^\circ - V_w \tag{4}$$

is plotted as a function of the intrinsic van der Waals volume V_w of the solute molecule. The straight lines reported for linear silicones and alkanes were calculated by a least-squares procedure. The V_w's of alkanes were obtained from the V_w increments in ref 25, and those of silicones, reported in Table 1, have been analytically computed by us using the Si atomic radius r_w = 0.210 nm[26] and bond lengths Si−C, l = 0.188 nm, and Si−O, l = 0.164 nm, reported in ref 27 for $SiMe_4$ and $Si(OMe)_4$, respectively. The method of calculation has been described in detail in ref 25. The V° of *n*-alkanes were taken from ref 28, those of cycloalkanes from ref 2, and branched alkanes from ref 1. The V° of silicones MD_4M and D_6 were obtained from eq 2 using V^* in Table 1 and $V^{E,\circ}$ = (0.7 and 1.0) $\mathrm{cm^3 \cdot mol^{-1}}$, respectively, estimated by us from $V^{E,\circ}$ in the homologous series. The V° of branched silicones TM_3 ($MeSi(OSiMe_3)_3$) and QM_4 ($Si(OSiMe_3)_4$) were obtained from V^* in Table 1 and assuming that $V_2^{E,\circ}$ is the same as the corresponding linear isomer.

It is evident from Figure 5 that, at a given V_w, linear silicones display V_e (and V°) values that are (15 to 40) $\mathrm{cm^3 \cdot mol^{-1}}$ larger than those of *n*-alkanes. This indicates that silicones are packed in heptane looser than alkanes, probably due to their bulky structure (see Figure 1), which needs a larger cavity to be accommodated in the solvent. This positive effect prevails on the negative one caused by the attractive interaction between the oxygen atoms in the silicone chain and heptane molecules. Likely, oxygen atoms are shielded by methyl groups in the silicone backbone, which practically prevent the O-solvent contacts. Larger V_e (and V°) than *n*-alkanes have been also observed for branched alkanes[1] and perfluoroalkanes.[29] These latter, like silicones, are inert molecules with a bulky shape and a homogeneous surface exposed to the solvent.

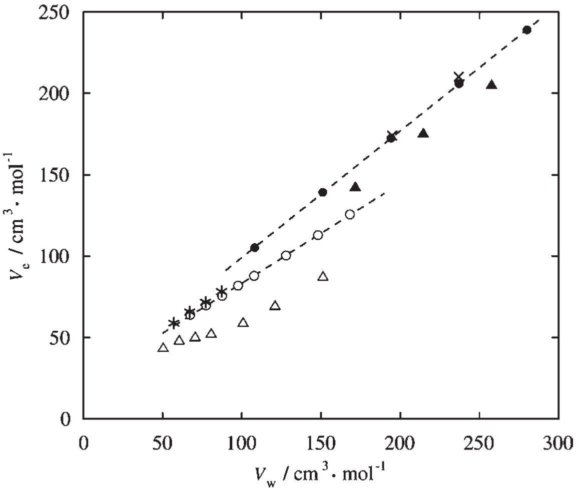

Figure 5. Empty volume V_e vs van der Waals volume of various compounds in heptane. ○, *n*-alkanes (C6−C10, C12, C14, C16); △, cyclic alkanes (C5−C8, C10, C12, C15); ∗, branched alkanes (2-methylbutane, 2,2-dimethylbutane, 2,2-dimethylpentane, 2,2,4-trimethylpentane); ●, linear silicones (from MM to MD_4M); ▲, cyclic silicones (D_4−D_6); ×, branched silicones (TM_3 and QM_4). Dashed lines represent best fitting straight lines.

The same figure also shows that cyclic silicones have V_e (and V°) about 10 $\mathrm{cm^3 \cdot mol^{-1}}$ lower than open chain ones, similarly to cycloalkanes having V_e about 20 $\mathrm{cm^3 \cdot mol^{-1}}$ lower than *n*-alkanes. This is due to the compact shape of cyclic molecules which require a smaller cavity inside the solvent structure. The need of a smaller space is also related to less degrees of freedom of a ring structure as compared to an extended one. In other words, an easier packing into the solvent structure for geometrical reasons may be responsible for the lower V_e and V° values of cyclic as compared with open chain compounds.[2] Finally, the branched silicones TM_3 and QM_4 have V_e (and V°) nearly 3 $\mathrm{cm^3 \cdot mol^{-1}}$ larger than linear isomers, similarly to branched alkanes as compared with *n*-alkanes.

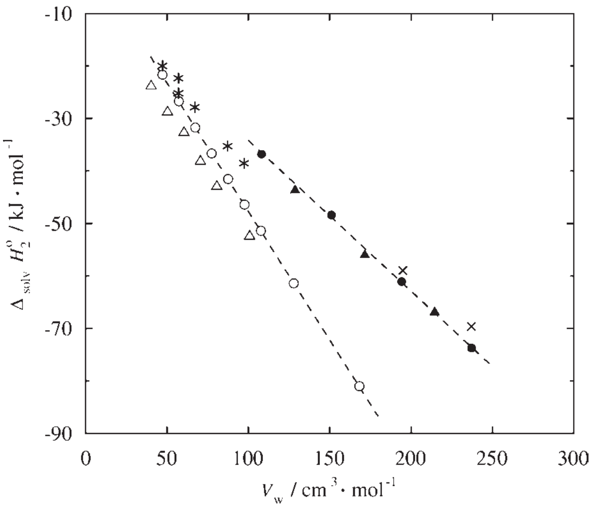

Figure 6. Standard enthalpy of solvation, $\Delta_{solv}H_2^\circ$, vs van der Waals volume of various compounds in heptane. ○, *n*-alkanes (C4−C10, C12, C16); △, cycloalkanes (C4−C8, C10); ∗, branched alkanes (2-methylpropane, 2,2-dimethylpropane, 2-methylbutane, 2,2-dimethylbutane, 2,2,4-trimethylpentane, 2,2,4,4-tetramethylpentane); ●, linear silicones (from MM to MD$_3$M); ▲, cyclic silicones (D$_3$−D$_5$); ×, branched silicones (TM$_3$, QM$_4$). Dashed lines represent best fitting straight lines.

This is due to the bulkier shape of branched silicones, which need a larger cavity to be accommodated into the solvent structure.

Enthalpies of Solvation. A graphical comparison of the solvation behavior of silicones and hydrocarbons in heptane is offered by Figure 6. The experimental $\Delta_{solv}H_2^\circ$ data, together with calculated straight lines, are plotted against the van der Waals volume V_w of the solutes. The $\Delta_{solv}H_2^\circ$ of alkanes (linear, cyclic, and branched) were taken from ref 18. The $\Delta_{solv}H_2^\circ$ of TM$_3$ and QM$_4$ were obtained from eq 3 using $\Delta_{vap}H_2^\circ$ in Table 1 and assuming that H_2° are the same as the corresponding linear isomers. The $\Delta_{solv}H_2^\circ$ of cyclic D$_3$ was calculated from $\Delta_{vap}H_2^\circ$ of Table 1, using an estimated value of $H_2^\circ = 2.3\ \mathrm{kJ \cdot mol^{-1}}$.

It is evident from Figure 6 that open chain silicones have $\Delta_{solv}H_2^\circ$ less negative than *n*-alkanes. The distance between the two straight lines varies from (13 to 30) kJ·mol^{-1}. This indicates that silicones, though containing oxygen atoms in the chain backbone, interact with the solvent more weakly than alkanes, probably because their bulky shape requires a larger solvent cavity for their accommodation and a looser packing. This positive packing effect, like in the case of the partial molar volumes, prevails on the negative one due to attractive interactions between the oxygen atoms of the silicone backbone and the solvent molecules. Likely, the oxygen atoms are almost completely shielded by methyl groups that hinder O-solvent contacts. A similar $\Delta_{solv}H_2^\circ$ behavior is exhibited by branched alkanes[18] and perfluoroalkanes,[30] both displaying $\Delta_{solv}H_2^\circ$ less negative than *n*-alkanes, the difference in $\Delta_{solv}H_2^\circ$ increasing with the branching of alkanes or with the size of perfluoroalkanes.

From Figure 6 it is also evident that cyclic silicones have a slightly more negative ((0 to 2) kJ·mol^{-1}) $\Delta_{solv}H_2^\circ$ than open chain ones, while cycloalkanes show $\Delta_{solv}H_2^\circ$ data about 7 kJ·mol^{-1} more negative than linear alkanes. Both branched silicones TM$_3$ and QM$_4$ exhibit less negative (3 kJ·mol^{-1}) $\Delta_{solv}H_2^\circ$ than linear silicone oligomers, similarly to branched alkanes with respect to *n*-alkanes. The negative effect of cyclization for silicones and alkanes is due, as in the case of V°, to the compact shape of cyclic molecules and to the consequent closer packing and stronger interaction with the solvent. A positive effect of branching on $\Delta_{solv}H_2^\circ$ has been observed also for amines and hydrocarbons[4] and can be ascribed to a looser packing of branched molecules in the solvent as compared to the linear ones.

Table 5. Group Contributions to the Partial Molar Volume ($Y = V_2^\circ$) and to the Solvation Enthalpy ($Y = \Delta_{solv}H_2^\circ$) for Silicone Oligomers in Heptane at 298.15 K

Y	A	B	σ^a	$[B/V_w]_{\mathrm{Me_2SiO}}$	$[B/V_w]_{\mathrm{CH_2}}$
$V_2^\circ/\mathrm{cm^3 \cdot mol^{-1}}$	137.26	76.50	0.21	1.78	1.59
$\Delta_{solv}H_2^\circ/\mathrm{kJ \cdot mol^{-1}}$	−24.18	−12.32	0.34	−0.28	−0.49

[a] Standard deviation of the fit of experimental data to eq 5.

Analysis in Terms of Group Contributions. Both V_e and $\Delta_{solv}H_2^\circ$ of linear silicones in heptane show a closely linear trend with V_w (see Figures 5 and 6) indicating a constant contribution by the repeating unit Me$_2$SiO. This behavior suggests the use of an additivity scheme for predicting V_2° and $\Delta_{solv}H_2^\circ$ of silicones in heptane based on eq 5

$$Y = A_Y + nB_Y \tag{5}$$

where $Y = V_2^\circ$, $\Delta_{solv}H_2^\circ$ of linear oligomers Me(Me$_2$SiO)$_n$-SiMe$_3$, A_Y is a constant term characteristic of the solvent which includes the contributions by the terminal groups Me and SiMe$_3$, and B_Y is the contribution by the repeating unit Me$_2$SiO appearing n times in the solute molecule. The B_Y value was computed as the average increment inside the homologous series of linear silicone oligomers. The constant term A_Y was obtained as a mean difference from experimental Y's using eq 5.

The results of the above calculations are summarized in Table 5. The V_2° were reproduced with a root-mean-square deviation of $\sigma = 0.2\ \mathrm{cm^3 \cdot mol^{-1}}$ and $\Delta_{solv}H_2^\circ$ with $\sigma = 0.3\ \mathrm{kJ \cdot mol^{-1}}$. The value of $B_V = 75.9\ \mathrm{cm^3 \cdot mol^{-1}}$ of the Me$_2$SiO group obtained from the V_2° values of the two cyclic silicones is very close to that of linear oligomers (76.5 cm^3·mol^{-1}).

The values $B_V = 76.5\ \mathrm{cm^3\ mol^{-1}}$ and $B_H = B_{\Delta H solv} = -12.3\ \mathrm{kJ \cdot mol^{-1}}$ obtained for the Me$_2$SiO group of linear silicones in heptane can be compared with the contribution by the CH$_2$ group of *n*-alkanes: $V^\circ(\mathrm{CH_2}) = 16.0\ \mathrm{cm^3 \cdot mol^{-1}}$[11] and $\Delta_{solv}H_2^\circ(\mathrm{CH_2}) = -4.96\ \mathrm{kJ \cdot mol^{-1}}$.[3] Evidently, the Me$_2$SiO contributions are larger in magnitude than those of CH$_2$, since B_Y increases with the group size. A more suitable comparison can be made by normalizing these contributions with respect to their van der Waals volumes, $V_w(\mathrm{Me_2SiO}) = 43.0\ \mathrm{cm^3 \cdot mol^{-1}}$ and $V_w(\mathrm{CH_2}) = 10.09\ \mathrm{cm^3 \cdot mol^{-1}}$. These relative quantities, reported in Table 5, indicate that the Me$_2$SiO group is more loosely packed than the CH$_2$ group in heptane, $[B_v/V_w]_{\mathrm{Me_2SiO}} > [B_v/V_w]_{\mathrm{CH_2}}$, and has a lower interaction capability with the solvent than CH$_2$, $[B_H/V_w]_{\mathrm{Me_2SiO}}$ less negative than $[B_H/V_w]_{\mathrm{CH_2}}$. It is to be noticed that B_H/V_w for Me$_2$SiO and CH$_2$ represent the slopes of the straight lines of linear silicones and *n*-alkanes, respectively (Figure 6).

Finally, to compare the volumetric behavior of oligomeric compounds in heptane with that of the silicone polymer (PDMS), values of the partial specific volume at infinite dilution in heptane, V_{sp}° (partial volume of one gram of solute), are plotted against the reciprocal molecular weight, 1/MW (Figure 7). The choice of 1/MW as abscissa allows a straightforward

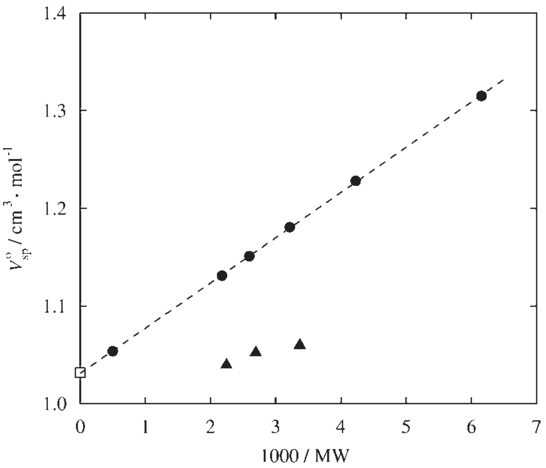

Figure 7. Partial specific volume at infinite dilution in heptane, $V_{sp}°$, vs reciprocal molecular weight (1/MW) for silicones: ●, linear silicones (from MM to MD_4M and PDMS); ▲, cyclic silicones (D_4−D_6); □, $V_{sp}°$ of the repeat unit Me_2SiO; - - -, best fitting straight line.

extrapolation to MW = ∞ since the function $V_{sp}° = f(1/MW)$ is linear when additivity rules hold for $V_2°$, as occurs for silicones and hydrocarbons. The intercept of the straight line represents the partial specific volume of the Me_2SiO group, whereas the slope is a composite quantity depending mainly upon the nature of the terminal groups. $V_{sp}°$ values of silicones approach 1.031 $cm^3 \cdot mol^{-1}$ as MW is increased. Multiplying this limiting value by the formula weight of Me_2SiO gives 76.45 $cm^3 \cdot mol^{-1}$, a value practically identical to that observed as mean increment from $V_2°$ data of the oligomers (76.5 $cm^3 \cdot mol^{-1}$). This value represents the partial molar volume of the repeat unit of a hypothetical polymer with MW = ∞. The $V_{sp}°$'s of cyclic silicones seem to approach the same limit, though with a different slope. It appears evident, therefore, that additivity holds for $V_2°$ of silicones over the whole molecular weight range explored, that is, the chain length does not affect the partial molar volume of the Me_2SiO unit, at least for molecular weights up to 2000.

Since the solute partial molar volume reflects solute−solvent interactions[25] in addition to its intrinsic volume, V_w, any conformational change which may alter the oxygen surface area exposed to solvent molecules and/or the packing of the Me_2SiO group in the solvent structure is expected to appreciably change its contribution to $V_2°$. The constancy of the $V°(Me_2SiO)$ contribution as the molecular size is increased is consistent with solute−solvent interactions that are independent of the polymerization degree. In other words, the Me_2SiO units in the examined polymer are accessible to the heptane molecules as easily as in oligomers, thus supporting an "open" or extended structure of the solvated polymer.

Estimate of the Average Separation of Solvent from Solute Molecules. To describe the partial molar volume, $V_2°$, of non polar spherical molecules, having a van der Waals radius r_w, the following expression has been used:[31]

$$V_2^{\circ} = 4/3\pi N(r_w + a)^3 \qquad (6)$$

It is supposed that the partial molar volume of a spherical solute molecule is equivalent to the volume of a sphere having a $(r_w + a)$ radius. The dead or void space around a solute particle corresponds to a hollow sphere of constant thickness a, independent of r_w, and is V_e defined in eq 4.

Table 6. Solute−Solvent Separation Distance, *a*, in Heptane and in MM

solute			in heptane		in MM	
	V_w	r_w	$V°$	a	$V°$	a
	$cm^3 \cdot mol^{-1}$	nm	$cm^3 \cdot mol^{-1}$	nm	$cm^3 \cdot mol^{-1}$	nm
MM	108.3	0.350	213.57	0.089	213.98	0.089
heptane	77.61	0.313	147.44	0.075	147.01	0.075

Using experimental $V°$ data in Table 3 and V_w values in Table 1, we have estimated the value of a for heptane and MM solutes each in both heptane and MM solvents. The radius r_w was calculated from V_w assuming a spherical solute. The results are reported in Table 6. The value of a, which measures the average separation of solvent from solute molecules, is larger for MM (0.089 nm) than for heptane (0.075 nm) both in heptane and in MM. Since the thickness of the spherical shell surrounding a solute molecule (eq 6) is practically independent of its size in a given solvent,[25,29] the above a values suggest that all silicones examined are more loosely packed than alkanes in both solvents. A larger a value indicates a weaker interaction, in agreement with the results obtained from $\Delta_{solv}H_2°$ data. A weaker interaction is also found in the gaseous state, where the virial coefficient of MM (−3.2 $dm^3 \cdot mol^{-1}$) is much smaller in magnitude than those of alkanes.[32]

■ CONCLUSIONS

For all silicones examined partial molar volumes, $V_2°$, in heptane are larger than those of alkanes of the same size. Analogously, the enthalpies of solvation in heptane, $\Delta_{solv}H_2°$, are less negative (smaller in magnitude) than those of alkanes, clearly indicating that solute−solvent interactions are weaker for silicones than for hydrocarbons. The enthalpies of vaporization, $\Delta_{vap}H_2°$, very close in magnitude to solvation enthalpies of silicones, are markedly lower than those of alkanes. The above-described behavior of $V_2°$, $\Delta_{solv}H_2°$, and $\Delta_{vap}H_2°$, which is similar to that of perfluoroalkanes, suggests that silicones are inert molecules that interact weakly with themselves as well as with hydrocarbons, the molecular interaction forces in the liquid state being in the order silicone−silicone ∼ silicone−alkane < alkane−alkane.

The weak interaction of silicones either with hydrocarbons and with themselves is mainly due to the bulky structure of these molecules, with the main chain of O and Si atoms being completely methylated. The silicone CH_3 groups bring about two effects: (i) they almost prevent oxygen-solvent contacts, and (ii) they cause a loose packing in the solvent structure. Both of these effects are responsible for the weak interaction of either hydrocarbon or silicone with the solvent.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Calorimetric experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

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